CATALYTIC ENANTIOSELECTIVE DIVERSITY-ORIENTED SYNTHESIS OF A SMALL LIBRARY OF POLYHYDROXYLATED PYRANS INSPIRED FROM THIOMARINOL ANTIBIOTICS

Supporting Information

Edmonton, Canada
[Pick the date]
Table of Contents

Table of Contents ............................................................. ii

1. Experimental Details and Compound Data................................................................. 1

1.1) General Information ................................................................................................... 1
1.2) Preparation of (Z)-1-ethoxyoct-1-ene (2c) ................................................................. 1
1.3) Preparation of (E)-3-borononacrolein ...................................................................... 2
1.4) Synthesis of (E)-3-borononacrolein pinacol ester (1) ................................................. 2
1.5) Synthesis of 2-((2S,4S)-2-ethoxy-3,4-dihydro-2H-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a) ................................................................. 3
1.6) Synthesis of 2-((2S,3R,4R)-2-ethoxy-3,4-dihydro-3-methyl-2H-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b) ................................................................. 3
1.7) Synthesis of 2-((2S,3R,4R)-2-ethoxy-3,4-dihydro-3-methyl-2H-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c) ................................................................. 4

2) General Procedure for Cr(III)-Catalyzed Three-Component [4+2] Allylation Using Ethyl Vinyl Ether 2a4

2.1) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(phenyl)methanol (6aa) ................................................................. 5
2.2) Synthesis of 4-((R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(hydroxy) methyl benzonitrile (6ab) ................................................................. 5
2.3) Synthesis of (R)-1-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)-3-phenyl propan-1-ol (6a) ................................................................. 6
2.4) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(p-tolyl)methanol (6ac) ................................................................. 6
2.5) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(o-tolyl)methanol (6ad) ................................................................. 6
2.6) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(4-nitrophenyl) methanol (6ae) ................................................................. 7
2.7) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(4-(trifluoro methyl) phenyl)methanol (6af) ................................................................. 7
2.8) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(4-fluorophenyl) methanol (6ag) ................................................................. 8
2.9) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(2-fluorophenyl) methanol (6ah) ................................................................. 8
2.10) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(naphtalen-2-yl) methanol (6ai) ................................................................. 9
2.11) Synthesis of (R)-((2-bromo-5-fluorophenyl)((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)methanol (6ak) ................................................................. 9
2.12) Synthesis of (R)-1-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)pentan-1-ol (6al) ................................................................. 10
2.13) Synthesis of (R)-cyclohexyl((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)methanol (6am) ................................................................. 10
2.15) Synthesis of 1-3-((R)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(Hydroxy)Methyl)-1H-Indol-1-yl)Ethanone (6ao) ................................................................. 11
2.16) Synthesis of (R)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(1-Methyl-1H-Pyrrol-2-yl)methanol (6ap) ................................................................. 11
2.17) Synthesis of (S)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(Furan-2-yl)methanol (6aq) ................................................................. 12
2.18) Synthesis of (S)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(Thiophen-2-yl)methanol (6ar) ................................................................. 12


3.1) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(phenyl) methanol (6ba) ................................................................. 13
3.2) Synthesis of 4-((R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(hydroxy)methyl)benzonitrile (6bb) ................................................................. 14
3.3) Synthesis of (R)-1-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)-3-phenylpropan-1-ol (6bi) ................................................................. 14
3.4) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(o-tolyl) methanol (6bg) ................................................................. 15
3.5) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(4-(trifluoromethyl) phenyl)methanol (6be) ................................................................. 15
3.6) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(4-fluorophenyl)methanol (6bf) ................................................................. 16
3.7) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(2-fluorophenyl)methanol (6bh) ................................................................. 16
3.8) Synthesis of (R)-((2-bromo-5-fluorophenyl)((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (6bk) ................................................................. 17
Supporting Information

4) General Procedure for Cr(III)-Catalyzed Three-Component [4+2]/ Allylation Using (Z)-1-Ethoxycyclopentene 3c ................................................................. 20

5) General Procedure for Acetal Reduction ................................................................................................................. 25

R. M. Al-Zoubi, and D. G. Hall
6) General Procedure for Dihydroxylation

6.1) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(phenyl)methyl)-2H-pyran-3,4-diol (8aa) ........................................... 38
6.2) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(p-cyanophenyl)methyl)-2H-pyran-3,4-diol (8ab) ......................... 38
6.3) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-1-hydroxy-3-phenylpropyl)-2H-pyran-3,4-diol (8al) ................................. 39
6.4) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(p-tolyl)methyl)-2H-pyran-3,4-diol (8ac) ................................. 39
6.5) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(o-tolyl)methyl)-2H-pyran-3,4-diol (8ag) ................................. 40
6.6) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(4-nitrophenyl)methyl)-2H-pyran-3,4-diol (8ad) ......................... 40
6.7) Synthesis of (2S,3R,4R)-2-((R)-4-(trifluoromethyl)phenyl)(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8ae) ......................... 41
6.8) Synthesis of (2S,3R,4R)-2-((R)-(4-fluorophenyl)(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8af) ......................... 41
6.9) Synthesis of (2S,3R,4R)-2-((R)-2-fluorophenyl)(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8ah) ......................... 42
6.10) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(naphthalen-2-yl)methyl)-2H-pyran-3,4-diol (8aj) ................. 42
6.12) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-1-hydroxypentyl)-2H-pyran-3,4-diol (8al) ........................................... 43
6.13) Synthesis of (2S,3R,4R)-2-((R)-cyclohexyl(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8am) ......................... 44
6.15) Synthesis of (2S,3R,4R,5S)-2-((R)-(4-cyanophenyl)(hydroxy)methyl)-tetrahydro-5-methyl-2H-pyran-3,4-diol (8ap) ................. 44
6.16) Synthesis of (2S,3R,4R,5S)-tetrahydro-2-((R)-1-hydroxy-3-phenylpropyl)-5-methyl-2H-pyran-3,4-diol (8aq) .......... 45
6.18) Synthesis of (2S,3R,4R,5S)-2-((R)-(4-trifluoromethyl)phenyl)(hydroxy)methyl)-tetrahydro-5-methyl-2H-pyran-3,4-diol (8as) ................. 46

General Synthesis of (Z,1R,2R)-6-Ethoxy-1-Phenylhex-3-ene-1,2-Diol (9aa) ........................................... 52

7) General Procedure for the Synthesis of Bicyclic Acetal Products ................................................................. 53

7.1) Synthesis of (1R,5R,7R)-7-Phenyl-6,8-Dioxa-Bicyclo[3.2.1]oct-2-ene (10aa) ........................................... 53
7.2) Synthesis of 4-((1R,5R,7R)-6,8-Dioxa-Bicyclo[3.2.1]oct-2-en-7-yl)Benzo Nitrile (10ab) ........................................... 53
7.3) Synthesis of N-((4-(1R,5R,7R)-6,8-Dioxa-Bicyclo[3.2.1]oct-2-en-7-yl)Phenyl) Acetamide (10an) ........54
7.4) Synthesis of (1R,4R,5R,7R)-7-(2-Fluorophenyl)-4-Methyl-6,8-Dioxa-Bicyclo[3.2.1]oct-2-ene (10bh) ....54
7.5) Synthesis of (1R,4R,5R,7R)-7-(4-Fluorophenyl)-4-Hexyl-6,8-Dioxa-Bicyclo[3.2.1]oct-2-ene (10cf) ....55
7.6) Synthesis of 4-((1R,4R,5R,7R)-4-Hexyl-6,8-Dioxa-Bicyclo[3.2.1]oct-2-en-7-yl)Benzonitrile (10cb) .......55
7.7) Synthesis of (1R,4R,5R,7R)-7-(4-{Trifluoromethyl}Phenyl)-4-Hexyl-6,8-Dioxa-Bicyclo[3.2.1]oct-2-ene (10ce) ....55

7. NMR Spectrum Data for New Compounds. ........................................................................................................57

8. X-ray Crystallographic Structure of Title Compound 6ad ..................................................................................142
1. Experimental Details and Compound Data

1.1) General Information

Catalyst 1 was prepared according to the procedure of Jacobsen.1 Boronate 3 was prepared according to our previously published procedure and purified by Kugelrohr distillation (< 0.5 mm Hg) (94%). Toluene and CH₂Cl₂ were distilled from CaH₂. Ethyl vinyl ether was stirred over KOH for 30 min. before distillation. All aldehydes were purified by Kugelrohr distillation prior to use. BaO (Acros) was used as supplied (90% tech powder). Powdered 4 Å molecular sieves (< 5 micron, Aldrich) were dried in a vacuum oven (138 °C) prior to use. Unless otherwise stated, all reagents were purchased from Aldrich and used as received. Analytical thin layer chromatography was performed on Merck Silica Gel 60 F254 plates and visualized with UV light and 1% KMnO₄(aq). NMR spectra were recorded on Varian INOVA-300, INOVA-400 or INOVA-500 MHz instruments. The residual solvent protons (¹H) or the solvent carbon (¹³C) were used as internal standards. ¹H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, integration, coupling constant). The following abbreviations are used in reporting NMR data: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; dq, doublet of quartets; dd, doublet of doublets; m, multiplet. High resolution mass spectra were recorded by the University of Alberta mass spectrum service laboratory using either electron impact (EI) or electrospray (ES) ionization techniques. Infrared spectra were obtained on a Nicolet Magna-IR 750 with frequencies expressed in cm⁻¹. Optical Rotations were measured using a 1 mL cell with a 1dm length on a P.E. 241 polarimeter.

1.2) Preparation of (Z)-1-ethoxyoct-1-ene (2c)

To a solution of sec-BuLi (1.4 M, 8.35 mL) in THF (10 mL) at -78 ºC was added dropwise the allyl ethyl ether (1.0 g, 11.6 mmol) and the mixture was stirred at -78 ºC for 1 h. 1-Iodopentane (1.4 g, 7.06 mmol) was added dropwise and the mixture was stirred for a further 3 h at -78 ºC. The reaction was then allowed to warm up to room temperature and then quenched with a saturated aqueous solution of NH₄Cl (10 mL). The resulting mixture was extracted with ether, organic layers were combined, dried over anhydrous MgSO₄, concentrated in vacuo and purified by flash chromatography (100% hexanes) to afford the title compound (0.89 g, 81 % yield).

1.3) Preparation of (E)-3-boronoacrolein

(R)-(+)-\(\alpha\)-pinene (91% ee, 10.8 mL, 66.7 mmol) was slowly added to a solution of borane-dimethyl sulfide complex (3.3 mL, 33.0 mmol) in THF (10 mL) at 0 °C under argon. The solution was stirred for 10 minutes at 0 °C followed by 2 hours at room temperature. The resulting white suspension was cooled to 0 °C and propioaldehyde diethyl acetal (4.50 mL, 31.0 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 hour and further stirred at room temperature for an additional hour, the reaction cooled back again to 0 °C prior to the quick addition of freshly distilled acetaldehyde (20 mL). The mixture was stirred for 30 minutes at 0 °C, then refluxed for 16 hours at 45 °C, water (12 mL) was added at 0 °C. After 3 hours, the solution was transferred to separatory funnel. The aqueous layer was extracted with ether (2 x 50 mL) and ethyl acetate (2 x 50 mL). The organic layers were combined and concentrated under reduced pressure. The resulting suspension was then triturated with cooled hexanes and filtered to provide the boronic acid as a white solid (2.66g, 81% yield).


1.4) Synthesis of (E)-3-boronoacrolein pinacol ester (1)

3-boronoacrolein (200 mg, 2.00 mmol) and pinacol were dissolved in THF (15 mL) at room temperature. The solution was stirred for 30 minutes then the solvent evaporated under reduced pressure at 45 °C to afford colorless oil. Addition of THF followed by concentration may be necessary to complete the condensation by azeotropic removal of the water. The crude oil was then purified by bulb to bulb distillation (1 mm Hg, 100 °C) to provide the aldehyde (364 mg, 100% yield).

1.5) Synthesis of 2-((2S,4S)-2-ethoxy-3,4-dihydro-2H-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a)

A mixture of 3-boronoacrolein pinacolate 1 (364 mg, 2.00 mmol) and ethyl vinyl ether 2a (1.9 mL, 20.0 mmol) was placed in an oven dried 10 ml RBF with stirbar. To this solution was added 4 (9.6 mg, 1 mol %) and powdered BaO (300 mg). The reaction was allowed to stir for 14 h at ambient temperature then filtered through celite and concentrated in vacuo to give crude product (427 mg, 84% yield, 96% dr).


1.6) Synthesis of 2-((2S,3R,4R)-2-ethoxy-3,4-dihydro-3-methyl-2H-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

A mixture of 3-boronoacrolein pinacolate 1 (364 mg, 2.00 mmol) and ethyl 1-propenyl ether 2b (Z/E 3:1) (2 mL) was placed in an oven dried 10 ml RBF with stirbar. To this solution was added 4 (30 mg, 3 mol %) and powdered BaO (300 mg). The reaction was allowed to stir for 14 h at ambient temperature then filtered through celite and concentrated in vacuo to give crude product (445 mg, 83% yield, 97% dr). 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.21 (dd, 1H, $J_1 = 6$, $J_2 = 2.4$ Hz), 4.76 (d, 1H, $J_1 = 2$ Hz), 4.75 (dd, 1H, $J_1 = 3.6$, $J_2 = 6$ Hz), 3.84 (dq, 1H, $J_1 = 9.6$, $J_2 = 7.2$ Hz), 3.84 (dq, 1H, $J_1 = 10$, $J_2 = 7.2$ Hz), 2.17 (m, 1H), 1.84 (m, 1H), 1.23 (d, 12H), 1.18 (dd, 3H, $J_1 = 2.4$, $J_2 = 4.4$ Hz), 1.04 (d, 3H, $J = 6.8$ Hz).
1.7) Synthesis of 2-((2S,3R,4R)-2-ethoxy-3,4-dihydro-3-methyl-2H-pyranyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)

A mixture of 3-boronoacrolein pinacolate 1 (364 mg, 2.00 mmol) and (Z)-1-ethoxyct-1-ene 2c (2 mL) was placed in an oven dried 10 mL RBF with stirbar. To this solution was added 4 (30 mg, 3 mol %) and powdered BaO (300 mg). The reaction was allowed to stir for 14 h at ambient temperature then filtered through celite and concentrated in vacuo and the excess of (Z)-1-ethoxyct-1-ene was recovered by bulb to bulb distillation to provide the title product. (478 mg, 71% yield, 99.5 % dr). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 6.20\ (dd, 1H, J = 6.5, 2.0 \text{ Hz}), 4.86 (dd, 1H, J = 5.5, 6 \text{ Hz}), 4.82 (d, 1H, J = 2 \text{ Hz}), 3.78 (dq, 1H, J = 10, 7 \text{ Hz}), 3.55 (dq, 1H, J = 10.5, 7.0 \text{ Hz}), 1.98 (m, 1H), 1.84 (m, 1H), 1.23 (d, 12H), 1.18 (dd, 3H, J = 2.4, 4.4 \text{ Hz}), 1.04(d, 3H, J = 6.8 \text{ Hz}).\(^{13}\)C NMR (MHz, CDCl\(_3\)) \(\delta 137.9, 104.0, 99.0, 82.8, 77.3, 77.0, 76.7, 63.3, 39.5, 31.7, 29.8, 29.8, 27.4, 25.1, 24.3, 22.6, 15.2, 14.1\)

2) General Procedure for Cr(III)-Catalyzed Three-Component [4+2]/Allyboration Using Ethyl Vinyl Ether 2a

A mixture of 3-boronoacrolein pinacolate 1 (364 mg, 2.00 mmol) and ethyl vinyl ether 2a (1.90 mL, 20.0 mmol) was placed in an oven dried 10 mL RBF with stirbar. To this solution was added 4 (9.6 mg, 1 mol %) and powdered 4Å M.S. (300mg). After stirred for 14 h at ambient temperature, aldehyde 3(a-t) (4.00 mmol) was added to the reaction mixture. The reaction mixture was allowed to stir at 45 °C for 24 h, then diluted with ethyl acetate and filtered through celite. The ethyl acetate solution was then stirred for 30 min. with a saturated solution of NaHCO\(_3\). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with saturated NaCl, dried over anhydrous MgSO\(_4\), filtered, and concentrated to afford title compound as a crude product.
Purification by automated flash chromatography (deactivated silica-gel, hexane:ether (9:1)) led to the pure product title compound.

2.1) Synthesis of \((R)-(2R,6S)-6\text{-ethoxy-5,6-dihydro-2H-pyran-2-yl})(\text{phenyl})\text{methanol (6aa)}

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl vinyl ether 2a (76% yield). \(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta: 7.35 \text{ (m, 5H), 5.77 \text{ (dddd, 1H, } J = 2.3Hz, J = 3.9Hz, J = 8.0Hz, J = 10.2Hz), 5.39 \text{ (ddd, 1H, } J = 2.1Hz, J = 3.9Hz, J = 10.3Hz), 4.78 \text{ (dd, 1H, } J = 5.0Hz, J = 5.4Hz), 4.58 \text{ (dd, 1H, } J = 2.7Hz, J = 7.5Hz), 4.33 \text{ (m, 1H), 3.98 \text{ (qd, 1H, } J = 7.1Hz, J = 9.6Hz), 3.58 \text{ (qd, 1H, } J = 7.1Hz, J = 9.6Hz), 3.28 \text{ (d, 1H, } J = 2.9Hz), 2.25 \text{ (m, 2H), 1.27 \text{ (dd, 3H, } J = 7.0Hz, J = 7.1Hz). \(^{13}\text{C NMR (125 MHz, CDCl}_3\) \(\delta: 139.9, 128.3, 128.0, 127.3, 125.4, 124.8, 98.5, 78.7, 76.8, 64.5, 31.0, 15.2. HRMS (ESI) for } C_{14}H_{18}NaO_3: \text{calcd. 257.11507; found, 257.11526.}}\)

2.2) Synthesis of \(4-((R)-(2R,6S)-6\text{-ethoxy-5,6-dihydro-2H-pyran-2-yl})(\text{hydroxy})\text{methyl})\text{benzonitrile (6ab)}

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl vinyl ether 2a (65% yield). \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta: 7.62 \text{ (dd, 2H, } J = 1.6Hz, J = 8.2Hz), 7.50 \text{ (m, 2H), 5.82 \text{ (ddddd, 1H, } J = 2.3Hz, J = 3.3Hz, J = 4.5Hz, J = 10.2Hz), 5.44 \text{ (ddd, 1H, } J = 1.9Hz, J = 3.9Hz, J = 10.3Hz), 4.73 \text{ (dd, 1H, } J = 4.0Hz, J = 6.4Hz), 4.65 \text{ (m, 1H), 4.35 \text{ (m, 1H), 3.85 \text{ (qd, 1H, } J = 7.1Hz, J = 9.5Hz), 3.51 \text{ (m, 2H), 2.21 \text{ (m, 2H), 1.21 \text{ (dd, 3H, } J = 7.0Hz, J = 7.1Hz). \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta: 145.9, 131.9, 127.7, 125.5, 124.8, 118.7, 111.5, 98.1, 77.8, 75.6, 64.5, 30.7, 15.1. HRMS (ESI) for } C_{15}H_{17}NNaO_3: \text{calcd. 282.11032; found, 282.11077.}}\)
2.3) Synthesis of (R)-1-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)-3-phenyl propan-1-ol (6ai)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylation using ethyl vinyl ether 2a (71% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.23 (m, 5H), 5.84 (m, 1H), 5.66 (ddd, 1H, \(J = 1.6\)Hz, \(J = 3.6\)Hz, \(J = 10.2\)Hz), 4.76 (m, 1H), 4.19 (m, 1H), 3.98 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.5\)Hz), 3.58 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.5\)Hz), 2.91 (m, 1H), 2.75 (m, 1H), 2.24 (m, 2H), 1.91 (m, 2H), 1.28 (dd, 1H, \(J = 7.0\)Hz, \(J = 7.1\)Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 142.1, 128.5, 128.3, 126.5, 125.8, 124.8, 98.4, 77.3, 72.6, 64.4, 35.0, 32.0, 31.0, 15.222. HRMS (ESI) for C\(_{16}\)H\(_{22}\)NaO\(_3\): calcd. 285.14645; found, 285.14673.

2.4) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(p-tolyl)methanol (6ac)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylation using ethyl vinyl ether 2a (38% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.28 (d, 2H, \(J = 8.1\)Hz), 7.16 (d, 2H, \(J = 7.8\)Hz), 5.74 (dddd, 1H, \(J = 3.9\)Hz, \(J = 3.9\)Hz, \(J = 10.2\)Hz), 5.38 (qd, 1H, \(J = 2.0\)Hz, \(J = 10.3\)Hz), 4.77 (m, 1H), 4.53 (d, 1H, \(J = 7.6\)Hz), 4.31 (m, 1H), 3.99 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.5\)Hz), 3.58 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.6\)Hz), 3.28 (bs, 1H), 2.34 (s, 1H), 2.23 (m, 2H), 1.27 (dd, 3H, \(J = 7.0\)Hz, \(J = 7.1\)Hz). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 137.6, 136.9, 129.0, 127.2, 125.5, 124.6, 98.4, 78.7, 76.6, 64.4, 31.0, 21.1, 15.2. HRMS (ESI) for C\(_{15}\)H\(_{20}\)NaO\(_3\): calcd. 271.13097; found, 271.13111.

2.5) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(o-tolyl)methanol (6ag)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylation using ethyl vinyl ether 2a (47% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.49 (dd, 1H, \(J = 1.5\)Hz, \(J = 7.6\)Hz), 7.23 (ddd, 1H, \(J =
1.7 Hz, J = 7.5 Hz, J = 7.5 Hz), 7.19 (ddd, 1H, J = 1.6 Hz, J = 7.3 Hz, J = 7.3 Hz), 7.15 (m, 1H), 5.75 (ddd, 1H, J = 2.3 Hz, J = 3.5 Hz, J = 4.5 Hz, J = 10.2 Hz), 5.28 (ddd, 1H, J = 2.1 Hz, J = 3.9 Hz, J = 10.3 Hz), 4.91 (d, 1H, J = 7.8 Hz), 4.80 (dd, 1H, J = 4.7 Hz, J = 6.2 Hz), 4.36 (m, 1H), 4.02 (qd, 1H, J = 7.1 Hz, J = 9.5 Hz), 3.61 (qd, 1H, J = 7.1 Hz, J = 9.5 Hz), 3.17 (s, 1H), 2.34 (s, 1H), 2.25 (m, 2H), 1.28 (dd, 3H, J = 7.0 Hz, J = 7.1 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 137.8, 135.7, 130.3, 127.7, 126.9, 126.1, 125.2, 124.9, 98.5, 78.9, 72.5, 64.4, 31.1, 19.7, 15.2. HRMS (ESI) for C$_{15}$H$_{20}$NaO$_3$: calcd. 271.13097; found, 271.13106.

2.6) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(4-nitrophenyl) methanol (6ad)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl vinyl ether 2a (62% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.20 (d, 2H, J = 8.8 Hz), 7.58 (d, 2H, J = 8.8 Hz), 5.85 (ddd, 1H, J = 2.2 Hz, J = 3.4 Hz, J = 4.3 Hz, J = 10.1 Hz), 5.49 (ddd, 1H, J = 2.0 Hz, J = 3.9 Hz, J = 10.3 Hz), 4.75 (dd, 1H, J = 4.2 Hz, J = 6.1 Hz), 4.72 (bs, 1H), 4.39 (m, 1H), 3.86 (qd, 1H, J = 7.1 Hz, J = 9.6 Hz), 3.52 (m, 2H), 2.24 (m, 2H), 1.23 (dd, 3H, J = 5.6 Hz, J = 8.7 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 147.9, 147.5, 127.8, 125.6, 124.7, 123.3, 98.0, 77.7, 75.4, 64.5, 30.6, 15.1. HRMS (ESI) for C$_{14}$H$_{17}$NNaO$_3$: calcd. 302.10037; found, 302.10089.

2.7) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(4-(trifluoromethyl) phenyl)methanol (6ae)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl vinyl ether 2a (75% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.63 (dd, 2H, J = 0.6 Hz, J = 8.1 Hz), 7.54 (dd, 2H, J = 0.6 Hz, J = 8.1 Hz), 5.83 (m, 1H), 5.44 (ddd, 1H, J = 1.9 Hz, J = 4.0 Hz, J = 10.1 Hz), 4.78 (dd, 1H, J = 4.3 Hz, J = 6.0 Hz), 4.66 (m, 1H), 4.36 (m, 1H), 3.93 (qd, 1H, J = 7.2 Hz, J = 15.4 Hz), 3.57 (qd, 1H, J = 7.1 Hz, J = 9.6 Hz), 3.36 (dd, 1H, J = 0.4 Hz, J = 3.9 Hz), 2.26 (m, 2H), 1.27 (dd, 3H, J = 7.0 Hz, J = 7.1 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 142.0, 131.1 (q, J = 30.2 Hz), 123.4, 125.4, 124.2,
124.284, 123.1 (q, J = 271.3Hz), 99.3, 77.3, 74.4, 63.5, 26.1, 14.1. HRMS (ESI) for C_{15}H_{17}F_{3}NaO_{3}: calcd. 325.10253; found, 325.10284.

2.8) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(4-fluorophenyl) methanol (6af)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl vinyl ether 2a (73% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.38 (ddd, 2H, \(J = 0.5\text{Hz}, J = 5.4\text{Hz}, J = 8.9\text{Hz}\)), 7.06 (dd, 2H, \(J = 8.8\text{Hz}, 8.7\text{Hz}\)), 5.79 (m, 1H), 5.38 (ddd, 1H, \(J = 2.1\text{Hz}, J = 3.9\text{Hz}, J = 10.3\text{Hz}\)), 4.78 (dd, 1H, \(J = 4.9\text{Hz}, J = 5.8\text{Hz}\)), 4.57 (dd, 1H, \(J = 2.3\text{Hz}, J = 7.3\text{Hz}\)), 4.29 (m, 1H), 3.97 (qd, 1H, \(J = 7.1\text{Hz}, J = 9.6\text{Hz}\)), 3.59 (qd, 1H, \(J = 7.1\text{Hz}, J = 9.5\text{Hz}\)), 3.26 (d, 1H, \(J = 2.8\text{Hz}\)), 2.26 (m, 2H), 1.28 (dd, 3H, \(J = 7.0\text{Hz}, J = 7.1\text{Hz}\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 166.0 (d, \(J = 242.3\text{Hz}\)), 135.9, 129.1 (d, \(J = 8.1\text{Hz}\)), 127.2, 125.8, 125.3 (d, \(J = 3.1\text{Hz}\)), 121.2, 115.4 (d, \(J = 21.3\text{Hz}\)), 98.6, 78.8, 76.3, 64.7, 31.2, 15.4. HRMS (ESI) for C_{14}H_{17}FNaO_{3}: calcd. 275.10576; found, 275.10591.

2.9) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(2-fluorophenyl) methanol (6ah)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl vinyl ether 2a (51% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.51 (ddd, 1H, \(J = 1.8\text{Hz}, J = 7.5\text{Hz}, J = 30.2\text{Hz}\)), 7.23 (m, 1H), 7.12 (ddd, 1H, \(J = 1.1\text{Hz}, J = 7.5\text{Hz}, J = 8.4\text{Hz}\)), 6.99 (ddd, 1H, \(J = 1.2\text{Hz}, J = 8.2\text{Hz}, J = 10.4\text{Hz}\)), 5.77 (ddddd, 1H, \(J = 2.3\text{Hz}, J = 3.5\text{Hz}, J = 4.4\text{Hz}, J = 10.2\text{Hz}\)), 5.46 (m, 1H), 4.95 (dd, 1H, \(J = 4.8\text{Hz}, J = 6.0\text{Hz}\)), 4.73 (dd, 1H, \(J = 4.5\text{Hz}, J = 6.2\text{Hz}\)), 4.40 (m, 1H), 3.88 (qd, 1H, \(J = 7.1\text{Hz}, J = 9.6\text{Hz}\)), 3.51 (qd, 1H, \(J = 7.2\text{Hz}, J = 9.6\text{Hz}\)), 3.46 (d, 1H, \(J = 4.6\text{Hz}\)), 2.21 (m, 2H), 1.20 (dd, 3H, \(J = 7.0\text{Hz}, J = 7.1\text{Hz}\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 159.937 (d, \(J = 244.7\text{Hz}\)), 129.1 (d, \(J = 8.2\)), 128.7 (d, \(J = 4.3\text{Hz}\)), 127.6 (d, \(J = 12.9\text{Hz}\)), 125.5, 125.0, 124.1 (d, \(J = 3.5\text{Hz}\)), 115.1 (d, \(J = 2.2\text{Hz}\)), 98.3, 77.7, 69.8, 64.3, 30.8, 15.1. HRMS (ESI) for C_{14}H_{17}FNaO_{3}: calcd. 275.10576; found, 275.10583.
2.10) Synthesis of (R)-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)(naphthalen-2-yl) methanol (6aj)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allyboration using ethyl vinyl ether 2a (81% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.85 (m, 4H), 7.54 (dd, 1H, $J = 1.7$Hz, $J = 8.5$Hz), 7.48 (m, 2H), 5.78 (m, 1H), 5.42 (ddd, 1H, $J = 2.0$Hz, $J = 4.0$Hz, $J = 10.3$Hz), 4.80 (dd, 1H, $J = 4.7$Hz, $J = 6.0$Hz), 4.76 (m, 1H), 4.45 (m, 1H), 4.00 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.59 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.43 (d, 1H, $J = 2.2$Hz), 2.25 (m, 2H), 1.28 (dd, 3H, $J = 7.0$Hz, $J = 7.1$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 137.4, 133.2, 133.2, 128.1, 128.0, 127.7, 126.5, 126.0, 125.9, 125.4, 125.0, 124.8, 98.4, 78.6, 76.9, 64.5, 31.0, 15.2. HRMS (ESI) for C$_{18}$H$_{20}$NaO$_3$: calcd. 307.13119; found, 307.13114.

2.11) Synthesis of (R)-(2-bromo-5-fluorophenyl)((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)methanol (6ak)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allyboration using ethyl vinyl ether 2a (49% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.47 (dd, 1H, $J = 5.2$Hz, $J = 8.8$Hz), 7.31 (dd, 1H, $J = 3.1$Hz, $J = 9.7$Hz), 6.88 (ddd, 1H, $J = 3.1$Hz, $J = 7.7$Hz, $J = 8.8$Hz), 5.88 (ddd, 1H, $J = 2.4$Hz, $J = 3.9$Hz, $J = 10.3$Hz), 5.62 (ddd, 1H, $J = 2.0$Hz, $J = 4.0$Hz, $J = 10.2$Hz), 5.03 (m, 1H), 4.75 (dd, 1H, $J = 4.8$Hz, $J = 5.7$Hz), 4.47 (m, 1H), 3.85 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.52 (m, 2H), 2.26 (m, 2H), 1.23 (dd, 3H, $J = 7.0$Hz, $J = 7.1$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 162.1 (d, $J = 245.4$Hz), 142.4, 142.3, 133.6, 133.5, 125.7, 125.3, 116.2 (d, $J = 23.6$Hz), 98.1, 76.6, 74.0, 64.5, 30.6, 15.1. HRMS (ESI) for C$_{14}$H$_{16}$BrNaO$_3$: calcd. 353.01653; found, 353.01642.
2.12) Synthesis of (R)-1-((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)pentan-1-ol (6al)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylation using ethyl vinyl ether $2a$ (81% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 5.76 (m, 1H), 5.61 (ddd, 1H, $J = 1.9$Hz, $J = 3.7$Hz, $J = 10.2$Hz), 4.69 (dd, 1H, $J = 4.9$Hz, $J = 6.1$Hz), 4.09 (m, 1H), 3.91 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.51 (m, 2H), 2.55 (bs, 1H), 2.16 (m, 2H), 1.10-1.90 (m, 6H), 1.20 (t, 3H, $J = 7.1$Hz), 0.86 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 126.6, 124.6, 98.4, 77.2, 73.3, 64.3, 32.6, 31.0, 27.8, 22.7, 15.1, 13.9. HRMS (ESI) for C$_{12}$H$_{22}$NaO$_3$: calcd. 237.14671; found, 237.14667.

2.13) Synthesis of (R)-cyclohexyl((2R,6S)-6-ethoxy-5,6-dihydro-2H-pyran-2-yl)methanol (6am)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylation using ethyl vinyl ether $2a$ (79% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 5.83 (dddd, 1H, $J = 2.4$Hz, $J = 3.6$Hz, $J = 4.3$Hz, $J = 10.1$Hz), 5.65 (ddd, 1H, $J = 2.0$Hz, $J = 3.7$Hz, $J = 10.1$Hz), 4.74 (dd, 1H, $J = 5.2$Hz, $J = 5.8$Hz), 4.37 (m, 1H), 3.95 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.56 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.23 (m, 1H), 2.24 (m, 3H), 1.97 (m, 1H), 1.40-1.87 (m, 6H), 1.25 (m, 7H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 127.7, 124.9, 98.7, 77.4, 74.7, 64.7, 40.5, 31.2, 29.8, 28.8, 26.6, 26.3, 26.1, 15.4. HRMS (ESI) for C$_{14}$H$_{24}$NaO$_3$: calcd. 263.16244; found, 263.16237.


The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylation using ethyl vinyl ether and N-(4-
formylphenyl)acetamide (36% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.62 (bs, 1H), 7.48 (d, 2H, \(J = 8.4 \text{ Hz}\)), 7.32 (d, 2H, \(J = 8.4 \text{ Hz}\)), 5.75 (m, 1H), 5.36 (ddd, 1H, \(J = 1.6 \text{ Hz}, J = 3.5 \text{ Hz}, J = 10.2 \text{ Hz}\)), 4.77 (dd, 1H, \(J = 5.4 \text{ Hz}, J = 5.3 \text{ Hz}\)), 4.53 (d, 1H, \(J = 7.4 \text{ Hz}\)), 4.29 (m, 1H), 3.97 (qd, 1H, \(J = 7.1 \text{ Hz}, J = 9.5 \text{ Hz}\)), 3.75 (bs, 1H), 2.23 (m, 2H), 2.14 (s, 3H), 1.25 (dd, 3H, \(J = 6.2 \text{ Hz}, J = 8.0 \text{ Hz}\)). \(^1\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 168.5, 137.7, 135.6, 127.9, 125.3, 124.8, 119.7, 98.4, 78.6, 64.5, 31.0, 24.8, 24.5, 15.2.

2.15) Synthesis of 1-(3-(((R)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(Hydroxy)Methyl)-1H-Indol-1-yl)Ethanone (6ao)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using ethyl vinyl ether and 1-acetyl-1H-indole-3-carbaldehyde (69% yield). \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.64 (ddd, 1H, \(J = 0.7 \text{ Hz}, J = 1.4 \text{ Hz}, J = 7.6 \text{ Hz}\)), 7.49 (s, 1H), 7.21-7.40 (m, 3H), 5.81 (dddd, 1H, \(J = 2.3 \text{ Hz}, J = 3.9 \text{ Hz}, J = 4.1 \text{ Hz}, J = 10.2 \text{ Hz}\)), 5.49 (ddd, 1H, \(J = 2.0 \text{ Hz}, J = 4.1 \text{ Hz}, J = 10.3 \text{ Hz}\)), 4.87 (d, 1H, \(J = 6.9 \text{ Hz}\)), 4.81 (dd, 1H, \(J = 5.3 \text{ Hz}, J = 5.4\)), 4.56 (m, 1H), 3.98 (qd, 1H, \(J = 7.1 \text{ Hz}, J = 9.5 \text{ Hz}\)), 3.59 (qd, 1H, \(J = 7.1 \text{ Hz}, J = 9.5 \text{ Hz}\)), 3.36 (bs, 1H), 2.59 (s, 3H), 2.27 (m, 2H), 1.22 (m, 3H). \(^1\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 168.5, 136.0, 135.0, 128.9, 126.8, 125.6, 125.4, 123.5, 123.6, 121.5, 119.8, 98.4, 77.7, 70.3, 64.5, 30.9, 23.9, 15.2.

2.16) Synthesis of (R)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(1-Methyl-1H-Pyrrol-2-yl)Methanol (6ap)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using ethyl vinyl ether and 1-methyl-1H-pyrrole-2-carbaldehyde (54% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\): 6.59 (dd, 1H, \(J = 1.8 \text{ Hz}, J = 2.6 \text{ Hz}\)), 6.16 (dd, 1H, \(J = 1.8 \text{ Hz}, J = 3.6 \text{ Hz}\)), 6.08 (dd, 1H, \(J = 2.7 \text{ Hz}, J = 3.6 \text{ Hz}\)), 5.78 (m, 1H), 5.52 (dd, 1H, \(J = 2.0 \text{ Hz}, J = 3.8 \text{ Hz}, J = 10.2 \text{ Hz}\)), 4.84 (dd, 1H, \(J = 4.8 \text{ Hz}, J = 6.4 \text{ Hz}\)), 4.62 (d, 1H, \(J = 7.5 \text{ Hz}\)), 4.57 (m, 1H), 4.04 (qd, 1H, \(J = 7.1 \text{ Hz}, J = 9.5 \text{ Hz}\)), 3.67 (s, 3H), 3.62
(qd, 1H, $J = 7.1$ Hz, $J = 9.5$ Hz), 2.98 (bs, 1H), 2.26 (m, 2H), 1.28 (t, 3H, $J = 7.1$ Hz). $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta$: 130.5, 126.2, 125.0, 123.0, 107.5, 106.8, 98.6, 76.8, 68.8, 64.5, 34.2, 31.1, 15.2.

2.17) Synthesis of (S)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl)(Furan-2-yl)Methanol (6a)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using ethyl vinyl ether and furan-2-carbaldehyde (59% yield). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.39 (dd, 1H, $J = 0.9$ Hz, $J = 1.8$ Hz), 6.36 (ddd, 1H, $J = 0.5$ Hz, $J = 0.9$ Hz, $J = 3.2$ Hz), 6.35 (dd, 1H, $J = 1.8$ Hz, $J = 3.3$ Hz), 5.81 (dddd, 1H, $J = 2.2$ Hz, $J = 3.3$ Hz, $J = 4.6$ Hz, $J = 10.2$ Hz), 5.47 (dddd, 1H, $J = 1.8$ Hz, $J = 4.1$ Hz, $J = 10.3$ Hz), 4.81 (dd, 1H, $J = 4.1$ Hz, $J = 6.4$ Hz), 4.62 (d, 1H, $J = 6.8$ Hz), 4.58 (m, 1H), 3.95 (qd, 1H, $J = 7.1$ Hz, $J = 9.6$ Hz), 3.56 (qd, 1H, $J = 7.1$ Hz, $J = 9.6$ Hz), 3.25 (bs, 1H), 2.25 (m, 2H), 1.25 (t, 3H, $J = 7.1$ Hz). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 153.1, 142.1, 125.2, 124.9, 110.2, 107.9, 98.2, 76.7, 70.3, 64.6, 30.9, 15.2. HRMS (ESI) for C$_{12}$H$_{16}$O$_4$: calcd. 224.10486; found, 224.10489.

2.18) Synthesis of (S)-((2R,6S)-6-Ethoxy-5,6-Dihydro-2H-Pyran-2-yl) (Thiophen-2-yl)Methanol (6ar)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using ethyl vinyl ether and thiophene-2-carbaldehyde (65% yield). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 7.28 (ddd, 1H, $J = 0.3$ Hz, $J = 1.2$ Hz, $J = 5.0$ Hz), 7.04 (ddd, 1H, $J = 0.7$ Hz, $J = 1.2$ Hz, $J = 3.5$ Hz), 6.97 (dd, 1H, $J = 3.5$ Hz, $J = 5.1$ Hz), 5.81 (dddd, 1H, $J = 2.3$ Hz, $J = 3.6$ Hz, $J = 4.1$ Hz, $J = 10.2$ Hz), 5.51 (dd, 1H, $J = 2.0$ Hz, $J = 4.1$ Hz, $J = 10.3$ Hz), 4.85 (d, 1H, $J = 6.7$ Hz), 4.80 (dd, 1H, $J = 4.6$ Hz, $J = 6.1$ Hz), 4.40 (m, 1H), 4.00 (qd, 1H, $J = 7.1$ Hz, $J = 9.6$ Hz), 3.58 (qd, 1H, $J = 7.1$ Hz, $J = 9.6$ Hz), 2.25 (m, 2H), 1.27 (t, 3H, $J = 7.1$ Hz). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 143.3, 126.4, 125.5, 125.3, 125.1, 98.4, 91.7, 78.3, 72.5, 64.6, 31.0, 15.3. HRMS (ESI) for C$_{12}$H$_{16}$O$_3$S: calcd. 240.08202; found, 240.08233.
3) General Procedure for Cr(III)-Catalyzed Three-Component [4+2]/Allyboration Using Ethyl 1-Propenyl Ether 2b

A mixture of 3-boronoacrolein pinacolate 1 (364 mg, 2.00 mmol) and ethyl 1-propenyl ether 2b (Z/E 3:1) (1.90 mL) was placed in an oven dried 10 mL RBF with stirbar. To this solution was added 4 (30 mg, 3 mol %) and powdered 4Å M.S. (300 mg). After stirred for 14 h at ambient temperature, the reaction mixture was diluted with ether and filtered over celite, concentrated under reduced pressure. The catalyst was removed through a short column (deactivated silica gel, hexane 100%).

A mixture of hetero-Diels-Alder cycloadduct and aldehyde (4.00 mmol) were stirred at 110 °C for 24 h under argon. After being cooled to room temperature, a saturated solution of NaHCO₃ was added to the reaction mixture was stirred for 30 minutes. The reaction mixture was extracted with ether (2 x 20 mL), the ethereal layers were combined and washed with saturated NaCl, dried over anhydrous MgSO₄, filtered, and concentrated to afford title compound as a crude product. Purification by automated flash chromatography (deactivated silica-gel, hexane:ether (9:1)) led to the pure product title compound.

3.1) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(phenyl) methanol (6ba)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allyboration using ethyl 1-propenyl ether 2b (79% yield). ¹H NMR (500 MHz, CDCl₃) δ: 7.35 (m, 5H), 5.74 (ddd, 1H, J = 2.4Hz, J = 4.6Hz, J = 10.2Hz), 5.34 (ddd, 1H, J = 1.7Hz, J = 1.7Hz, J = 10.2Hz), 4.74 (d, 1H, J = 3.3Hz), 4.56 (dd, 1H, J = 2.9Hz, J = 7.4Hz), 4.33 (m, 1H), 3.97 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 3.57 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 3.40 (d, 1H, J = 2.9Hz), 2.32 (m, 1H), 1.27 (dd, 3H, J = 7.0Hz, J = 7.1Hz), 1.06 (d, 3H, J = 7.0Hz). ¹³C NMR (125 MHz, CDCl₃) δ: 140.0, 131.4, 128.3, 127.9, 127.2, 124.2, 100.0, 78.7, 76.8, 64.6, 33.7, 15.1, 13.9. HRMS (ESI) for C₁₅H₂₀NaO₅: calcd. 271.13119; found, 271.13107.
3.2) Synthesis of 4-((R)-(2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl) (hydroxy)methyl)benzonitrile (6bb)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylaboration using ethyl 1-propenyl ether 2b (50% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.64 (dd, 2H, $J = 1.6$Hz, $J = 6.4$Hz), 7.50 (m, 2H), 5.77 (ddd, 1H, $J = 2.4$Hz, $J = 4.4$Hz, $J = 10.1$Hz), 5.42 (ddd, 1H, $J = 2.0$Hz, $J = 4.2$Hz, $J = 10.4$Hz), 4.68 (d, 1H, $J = 13.6$Hz), 4.63 (dd, 1H, $J = 2.8$Hz, $J = 8.4$Hz), 4.34 (m, 1H), 3.86 (qd, 1H, $J = 6.8$Hz, $J = 9.6$Hz), 3.55 (d, 1H, $J = 5.2$Hz), 3.53 (qd, 1H, $J = 7.2$Hz, $J = 9.7$Hz), 2.35 (m, 1H), 1.23 (dd, 3H, $J = 7.0$Hz, $J = 7.1$Hz), 0.99 (d, 3H, $J = 7.2$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 146.1, 131.9, 127.7, 123.6, 118.8, 111.4, 99.7, 77.7, 75.6, 64.9, 33.4, 15.0, 14.0. HRMS (ESI) for C$_{16}$H$_{19}$NNaO$_3$: calcd. 296.12632; found, 296.12628.

3.3) Synthesis of (R)-1-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)-3-phenylpropan-1-ol (6bi)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylaboration using ethyl 1-propenyl ether 2b (65% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.23 (m, 5H), 5.81 (ddd, 1H, $J = 2.4$Hz, $J = 4.7$Hz, $J = 10.2$Hz), 5.60 (ddd, 1H, $J = 1.7$Hz, $J = 1.7$Hz, $J = 10.2$Hz), 4.72 (d, 1H, $J = 3.3$Hz), 4.18 (m, 1H), 3.95 (qd, 1H, $J = 7.1$Hz, $J = 9.7$Hz), 3.57 (m, 2H), 2.90 (m, 1H), 2.74 (m, 2H), 2.32 (m, 1H), 1.90 (m, 2H), 1.26 (dd, 3H, $J = 7.0$Hz, $J = 7.1$Hz), 1.06 (d, 3H, $J = 7.0$Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 142.2, 131.5, 128.5, 128.3, 125.7, 125.3, 100.0, 77.5, 72.6, 64.6, 35.0, 33.8, 32.0, 15.1, 13.9. HRMS (ESI) for C$_{17}$H$_{24}$NaO$_5$: calcd. 299.16177; found, 299.16139.
3.4) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(o-tolyl) methanol (6bg)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl 1-propenyl ether 2b (63% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.48 (dd, 1H, $J = 1.7$Hz, $J = 7.5$Hz), 7.18 (m, 3H), 5.72 (dddd, 1H, $J = 0.7$Hz, $J = 2.4$Hz, $J = 4.8$Hz, $J = 10.2$Hz), 5.22 (ddd, 1H, $J = 1.7$Hz, $J = 1.7$Hz, $J = 10.2$Hz), 4.88 (d, 1H, $J = 7.7$Hz), 4.74 (dddd, 1H, $J = 0.6$Hz, $J = 3.2$Hz), 4.34 (m, 1H), 4.00 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.59 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.14 (bs, 1H), 2.33 (s, 3H), 2.30 (m, 1H), 1.26 (dd, 1H, $J = 7.0$Hz, $J = 14.0$Hz), 1.06 (d, 1H, $J = 7.0$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 138.0, 135.7, 131.5, 130.3, 127.6, 126.8, 126.1, 124.1, 100.1, 79.1, 72.7, 64.5, 60.3, 33.8, 19.7, 15.1, 14.1. HRMS (ESI) for C$_{16}$H$_{22}$NaO$_3$: calcd. 285.14671; found, 285.14668.

3.5) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(4- (trifluoromethyl) phenyl)methanol (6be)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl 1-propenyl ether 2b (93% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.61 (d, 2H, $J = 8.1$Hz), 7.52 (dd, 2H, $J = 0.6$Hz, $J = 8.0$Hz), 5.77 (dddd, 1H, $J = 2.4$Hz, $J = 4.4$Hz, $J = 10.3$Hz), 5.39 (dddd, 1H, $J = 1.8$Hz, $J = 1.8$Hz, $J = 10.3$Hz), 4.71 (d, 1H, $J = 3.4$Hz), 4.64 (dd, 1H, $J = 3.4$Hz, $J = 6.4$Hz), 4.35 (dddd, 1H, $J = 2.4$Hz, $J = 4.8$Hz, $J = 6.5$Hz), 3.92 (qd, 1H, $J = 7.1$Hz, $J = 9.7$Hz), 3.54 (m, 2H), 2.33 (m, 1H), 1.25 (dd, 3H, $J = 7.0$Hz, $J = 7.1$Hz), 1.04 (d, 3H, $J = 7.1$Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 144.5, 131.7, 129.9 (q, $J = 32.3$Hz), 127.4, 125.1 (q, $J = 3.6$Hz), 124.1 (q, $J = 271.6$Hz), 123.8, 99.9, 78.1, 75.9, 64.8, 33.6, 15.0, 13.9. HRMS (ESI) for C$_{16}$H$_{19}$F$_3$NaO$_3$: calcd. 339.11785; found, 339.11800.
3.6) Synthesis of \((R)\)-\(((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(4-fluorophenyl) methanol\) (6bf)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component \([4+2]/\)allylaboration using ethyl 1-propenyl ether \(2b\) (97% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.35 (m, 2H), 7.02 (ddd, 1H, \(J = 2.5\)Hz, \(J = 5.9\)Hz, \(J = 10.8\)Hz), 5.73 (ddd, 1H, \(J = 2.4\)Hz, \(J = 4.6\)Hz, \(J = 10.2\)Hz), 5.31 (ddd, 1H, \(J = 1.7\)Hz, \(J = 1.7\)Hz, \(J = 10.2\)Hz), 4.71 (d, 1H, \(J = 3.3\)Hz), 4.53 (d, 1H, \(J = 7.2\)Hz), 4.27 (ddd, 1H, \(J = 2.5\)Hz, \(J = 4.5\)Hz, \(J = 7.1\)Hz), 3.93 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.7\)Hz), 3.55 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.7\)Hz), 3.45 (bs, 1H), 2.30 (m, 1H), 1.24 (dd, 1H, \(J = 7.0\)Hz, \(J = 7.1\)Hz), 1.02 (d, 1H, \(J = 7.0\)Hz). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 162.4 (d, \(J = 245.3\)Hz), 135.9 (d, \(J = 3.4\)Hz), 131.6, 128.8 (d, \(J = 8.0\)Hz), 123.9, 115.1 (d, \(J = 21.4\)Hz), 100.0, 78.6, 76.0, 64.6, 33.7, 15.1, 13.8. HRMS (ESI) for C\(_{15}\)H\(_{19}\)FNaO\(_5\): calcd. 289.12104; found, 289.12115.

3.7) Synthesis of \((R)\)-\(((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)(2-fluorophenyl)methanol\) (6bb)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component \([4+2]/\)allylaboration using ethyl 1-propenyl ether \(2b\) (59% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.54 (ddd, 1H, \(J = 1.8\)Hz, \(J = 7.5\)Hz, \(J = 7.5\)Hz), 7.26 (dddd, 1H, \(J = 1.9\)Hz, \(J = 5.3\)Hz, \(J = 7.2\)Hz, \(J = 8.2\)Hz), 7.16 (ddd, 1H, \(J = 1.2\)Hz, \(J = 7.5\)Hz, \(J = 7.5\)Hz), 7.02 (ddd, 1H, \(J = 1.2\)Hz, \(J = 8.2\)Hz, \(J = 10.5\)Hz), 5.78 (ddd, 1H, \(J = 2.4\)Hz, \(J = 4.4\)Hz, \(J = 10.2\)Hz), 5.45 (ddd, 1H, \(J = 1.7\)Hz, \(J = 2.9\)Hz, \(J = 10.2\)Hz), 4.94 (d, 1H, \(J = 6.1\)Hz), 4.51 (d, 1H, \(J = 3.3\)Hz), 4.45 (m, 1H), 3.93 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.7\)Hz), 3.54 (qd, 1H, \(J = 7.1\)Hz, \(J = 9.7\)Hz), 3.40 (bs, 1H), 2.32 (m, 1H), 1.25 (dd, 1H, \(J = 7.0\)Hz, \(J = 7.1\)Hz), 1.06 (d, 1H, \(J = 7.1\)Hz). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 159.9 (d, \(J = 244.5\)Hz), 131.5, 129.1 (d, \(J = 8.2\)Hz), 128.6 (d, \(J = 4.3\)Hz), 127.7 (d, \(J = 12.9\)Hz), 124.3, 124.0 (d, \(J = 3.4\)Hz), 115.1 (d, \(J = 21.9\)Hz), 99.8, 77.6, 70.1, 64.7, 33.6, 15.0, 14.0. HRMS (ESI) for C\(_{15}\)H\(_{19}\)FNaO\(_5\): calcd. 289.12104; found, 289.12112.
3.8) Synthesis of (R)-(2-bromo-5-fluorophenyl)((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (6bk)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl 1-propenyl ether 2b (53% yield). ¹H NMR (500 MHz, CDCl₃) δ: 7.48 (dd, 1H, J = 5.2Hz, J = 8.7Hz), 7.31 (dd, 1H, J = 3.1Hz, J = 9.7Hz), 6.88 (ddd, 1H, J = 3.1Hz, J = 7.7Hz, J = 8.7Hz), 5.83 (ddd, 1H, J = 2.5Hz, J = 4.2Hz, J = 10.2Hz), 5.60 (ddd, 1H, J = 1.8Hz, J = 10.2Hz, J = 10.2Hz), 4.99 (dd, 1H, J = 4.7Hz, J = 4.8Hz), 4.70 (d, 1H, J = 3.4Hz), 4.52 (m, 1H), 3.90 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 3.73 (d, 1H, J = 5.7Hz), 3.55 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 2.34 (m, 1H), 1.25 (dd, 1H, J = 7.1Hz, J = 7.0Hz), 1.08 (d, 1H, J = 7.1Hz). ¹³C NMR (125 MHz, CDCl₃) δ: 162.1 (d, J = 246.3Hz), 142.6 (d, J = 6.9Hz), 133.6 (d, J = 7.6Hz), 131.7, 124.6, 116.2 (d, J = 1.8Hz), 116.0 (d, J = 5.6Hz), 99.7, 76.4, 74.0, 65.1, 33.4, 15.0, 14.2. HRMS (ESI) for C₁₅H₁₈FBrNaO₃: calcd. 367.03261; found, 367.03288.

3.9) Synthesis of (R)-1-((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)pentan-1-ol (6bl)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl 1-propenyl ether 2b (74 % yield). ¹H NMR (500 MHz, CDCl₃) δ: 5.77 (ddd, 1H, J = 2.4Hz, J = 4.7Hz, J = 10.2Hz), 5.58 (ddd, 1H, J = 1.7Hz, J = 1.7Hz, J = 10.2Hz), 4.67 (d, 1H, J = 3.3Hz), 4.11 (ddd, 1H, J = 1.7Hz, J = 2.7Hz, J = 5.1Hz), 3.90 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 3.52 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 3.49 (bs, 1H), 2.27 (m, 1H), 2.58 (d, 1H, J = 4.0Hz), 1.50 (m, 2H), 1.33 (m, 4H), 1.21 (dd, 3H, J = 7.1Hz, J = 7.0Hz), 1.01 (d, 3H, J = 7.0Hz), 0.89 (t, 3H, J = 7.2Hz). ¹³C NMR (125 MHz, CDCl₃) δ: 131.3, 125.4, 100.0, 77.4, 73.3, 64.5, 33.8, 32.7, 27.8, 22.7, 15.0, 14.0, 13.8. HRMS (ESI) for C₁₃H₂₄NaO₃: calcd. 251.16239; found, 251.16256.
3.10) Synthesis of (R)-cyclohexyl((2R,5R,6S)-6-ethoxy-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (6bm)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using ethyl 1-propenyl ether 2b (59% yield). \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\): 5.79 (ddd, 1H, \(J = 2.5\) Hz, \(J = 4.7\) Hz, \(J = 10.2\) Hz), 5.58 (ddd, 1H, \(J = 1.7\) Hz, \(J = 1.7\) Hz, \(J = 10.2\) Hz), 4.68 (d, 1H, \(J = 3.3\) Hz), 4.35 (m, 1H), 3.91 (qd, 1H, \(J = 7.1\) Hz, \(J = 9.7\) Hz), 3.53 (qd, 1H, \(J = 7.1\) Hz, \(J = 9.7\) Hz), 3.18 (m, 1H), 2.38 (m, 1H), 2.28 (m, 1H), 1.96 (m, 1H), 1.40-1.96 (m, 6H), 1.23 (dd, 3H, \(J = 7.0\) Hz, \(J = 7.1\) Hz), 1.00-1.23 (m, 4H), 1.03 (d, 3H, \(J = 7.0\) Hz). \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\): 131.2, 126.2, 99.9, 77.4, 74.6, 64.6, 40.3, 33.6, 29.6, 28.5, 26.4, 26.3, 26.1, 15.0, 13.9. HRMS (ESI) for C\(_{15}\)H\(_{26}\)NaO\(_3\): calcd. 277.17742; found, 277.17697.


The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using ethyl 1-propenyl ether and furan-2-carbaldehyde (58% yield). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.39 (dd, 1H, \(J = 0.9\) Hz, \(J = 1.8\) Hz), 6.35 (m, 1H), 5.76 (ddd, 1H, \(J = 2.2\) Hz, \(J = 4.3\) Hz, \(J = 10.3\) Hz), 5.42 (td, 1H, \(J = 1.7\) Hz, \(J = 10.2\) Hz), 4.75 (d, 1H, \(J = 3.4\) Hz), 4.58 (m, 1H), 3.94 (qd, 1H, \(J = 7.1\) Hz, \(J = 9.7\) Hz), 3.55 (qd, 1H, \(J = 7.1\) Hz, \(J = 9.7\) Hz), 3.38 (d, 1H, \(J = 4.1\) Hz), 2.35 (m, 1H), 1.24 (t, 3H, \(J = 7.1\) Hz), 1.04 (d, 3H, \(J = 7.1\) Hz). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 153.3, 142.1, 131.4, 124.0, 110.2, 107.8, 99.8, 76.0, 70.3, 64.7, 33.5, 15.0, 14.0. HRMS (ESI) for C\(_{13}\)H\(_{18}\)NaO\(_3\): calcd. 261.10973; found. 261.10928.


The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using ethyl 1-propenyl ether

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component \([4+2]\) cycloaddition/allylation using ethyl 1-propenyl ether and 2-hexenal (63% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\): 5.76 (m, 2H), 5.57 (td, 1H, \(J = 1.7\) Hz, \(J = 10.2\) Hz), 5.48 (tdd, 1H, \(J = 1.5\) Hz, \(J = 7.3\) Hz, \(J = 15.4\) Hz), 4.70 (d, 1H, \(J = 3.3\) Hz), 4.08 (m, 1H), 3.93 (m, 2H), 3.53 (qd, 1H, \(J = 7.1\) Hz, \(J = 9.7\) Hz), 2.90 (d, 1H, \(J = 3.3\) Hz), 2.29 (m, 1H), 1.40 (m, 2H), 1.23 (t, 5H, \(J = 7.1\) Hz), 1.02 (d, 3H, \(J = 7.0\) Hz), 0.89 (t, 3H, \(J = 7.4\) Hz). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\): 134.8, 131.1, 128.3, 124.6, 100.0, 77.7, 75.1, 64.5, 34.4, 33.7, 22.1, 15.0, 13.8, 13.6. HRMS (ESI) for C\(_{14}\)H\(_{24}\)NaO\(_3\): calcd. 263.16177; found. 263.16185.


The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component \([4+2]\) cycloaddition/allylation using ethyl 1-propenyl ether and 3-(5-methylfuran-2-yl)butanal (70% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\): 5.85 (dd, 1H, \(J = 3.0\) Hz, \(J = 10.2\) Hz), 5.81 (m, 1H), 5.77 (m, 1H), 5.56 (tdd, 1H, \(J = 1.6\) Hz, \(J = 10.2\) Hz, \(J = 13.5\) Hz), 4.68 (dd, 1H, \(J = 3.3\) Hz, \(J = 11.2\) Hz), 4.10 (m, 1H), 3.91 (dqq, 1H, \(J = 4.3\) Hz, \(J = 7.1\) Hz, \(J = 9.7\) Hz), 3.62 (bs, 1H), 3.51 (m, 2H), 3.07 (m, 1H), 2.28 (m, 1H), 1.62 (t, 3H, \(J = 7.1\) Hz), 1.14 (d, 3H, \(J = 7.1\) Hz), 0.89 (t, 3H, \(J = 7.4\) Hz).
2.21 (s, 3H), 1.10-1.30 (m, 8H), 1.02 (dd, 3H, \( J = 6.9 \) Hz, \( J = 9.4 \) Hz). \(^{13}\text{C-NMR} (100 \text{ MHz, CDCl}_3) \delta: 158.8, 157.9, 150.0, 131.3, 125.5, 105.6, 104.6, 103.8, 99.9, 77.8, 77.4, 71.4, 70.8, 64.5, 33.7, 15.0, 13.4. \text{HRMS} (\text{ESI}) \text{ for C}_{17}\text{H}_{26}\text{O}_4: \text{calcd. 294.18311; found. 294.18319.}

4) General Procedure for Cr(III)-Catalyzed Three-Component [4+2]/Allylboration Using (Z)-1-Ethoxyoct-1-ene 3c

A mixture of 3-boronoacrolein pinacolate 1 (364mg, 2.00 mmol) and ethyl (Z)-1-ethoxyoct-1-ene 2c (2.0 mL) was placed in an oven dried 10 mL RBF with stirbar. To this solution was added 4 (30 mg, 3 mol %) and powdered 4Å M.S. (300mg). After stirred for 14 h at ambient temperature, the reaction mixture was diluted with ether and filtered over celite, concentrated under reduced pressure. The catalyst was removed through a short column (deactivated silica gel, hexane 100%), and the excess of (Z)-1-ethoxyoct-1-ene was partly recovered by bulb to bulb distillation to provide the hetero-Diels-Alder cycloadduct product.

A mixture of hetero-Diels-Alder cycloadduct and aldehyde (4.00 mmol) were stirred at 110 °C for 24 h under argon. After being cooled to room temperature, a saturated solution of NaHCO\(_3\) was added to the reaction mixture was stirred for 30 minutes. The reaction mixture was extracted with ether (2 x 20 mL), the ethereal layers were combined and washed with saturated NaCl, dried over anhydrous MgSO\(_4\), filtered, and concentrated to afford title compound as a crude product. Purification by automated flash chromatography (deactivated silica-gel, hexane:ether (9:1)) led to the pure product title compound.

4.1) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)(phenyl) methanol (6ca)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using (Z)-1-ethoxyoct-1-ene 3c (79% yield). \(^{1}\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta: 7.33 \text{ (m, 5H), 5.78 (ddd, 1H, } J = 2.4 \text{Hz, } J = 4.1 \text{Hz, } J = 10.4 \text{Hz), 5.39 (ddd, 1H, } J = 1.9 \text{Hz, } J = 1.9 \text{Hz, } J
= 10.4Hz), 4.76 (d, 1H, J = 3.4Hz), 4.57 (d, 1H, J = 7.4Hz), 4.33 (ddd, 1H, J = 2.3Hz, J = 5.0Hz, J = 7.3Hz), 3.96 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.55 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.50 (bs, 1H), 2.23 (m, 1H), 0.75-1.80 (m, 16H). 13C NMR (100 MHz, CDCl3) δ: 140.2, 129.6, 128.2, 127.8, 127.1, 124.4, 99.7, 78.4, 76.7, 64.6, 46.1, 38.6, 31.7, 29.5, 26.8. HRMS (ESI) for C20H30NaO3: calcd. 341.20931; found, 341.20965

3.2) Synthesis of 4-((R)-(2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)(hydroxy)methyl)benzonitrile (6cb)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using (Z)-1-ethoxyoct-1-ene 3c (72% yield). 1H NMR (400 MHz, CDCl3) δ: 7.63 (d, 1H, J = 8.3Hz), 7.51 (d, 1H, J = 8.6Hz), 5.82 (ddd, 1H, J = 2.5Hz, J = 3.8Hz, J = 10.4Hz), 5.46 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.4Hz), 4.72 (d, 1H, J = 3.6Hz), 4.65 (d, 1H, J = 5.8Hz), 4.38 (ddd, 1H, J = 2.3Hz, J = 5.5Hz), 3.87 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.67 (bs, 1H), 3.50 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 2.22 (m, 1H), 1.10-1.70 (m, 13H), 0.87 (m, 1H). 13C NMR (100 MHz, CDCl3) δ: 146.3, 131.9, 130.3, 127.6, 123.8, 118.7, 111.3, 99.3, 77.4, 75.5, 64.9, 38.3, 31.7, 31.5, 29.5, 29.4, 26.7, 22.5, 15.0, 14.0. HRMS (ESI) for C21H29NNaO3: calcd. 366.20449; found, 366.20476.

4.3) Synthesis of (R)-1-((2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)-3-phenylpropan-1-ol (6ci)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/allylboration using (Z)-1-ethoxyoct-1-ene 3c (65% yield). 1H NMR (400 MHz, CDCl3) δ: 7.10-7.45 (m, 5H), 5.87 (ddd, 1H, J = 2.4Hz, J = 4.3Hz, J = 10.3Hz), 5.65 (ddd, 1H, J = 1.8Hz, J = 1.8Hz, J = 10.3Hz), 4.75 (d,
1H, $J = 3.5$Hz), 4.19 (m, 1H), 3.95 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.56 (m, 2H), 2.91 (m, 1H), 2.75 (ddd, 1H, $J = 7.3$Hz, $J = 9.4$Hz, $J = 13.8$Hz), 2.24 (s, 1H), 1.90 (m, 2H), 1.13-1.62 (m, 10H), 1.26 (t, 1H, $J = 7.1$Hz), 0.92 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 142.2, 129.7, 128.5, 128.3, 125.7, 125.5, 99.7, 77.2, 72.6, 64.7, 38.7, 35.1, 32.0, 31.8, 29.5, 29.5, 26.9, 22.6, 15.0, 14.1. HRMS (ESI) for C$_{22}$H$_{34}$NaO$_3$: calcd. 369.24061; found, 369.24048.

4.4) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)(4-(trifluoromethyl)phenyl)methanol (6ce)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/ allylboration using (Z)-1-ethoxyoct-1-ene 3b (67% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.62 (d, 1H, $J = 8.1$Hz), 7.53 (d, 1H, $J = 8.6$Hz), 5.83 (ddd, 1H, $J = 2.5$Hz, $J = 3.9$Hz, $J = 10.4$Hz), 5.46 (ddd, 1H, $J = 2.0$Hz, $J = 2.0$Hz, $J = 10.4$Hz), 4.76 (d, 1H, $J = 3.5$Hz), 4.66 (d, 1H, $J = 6.4$Hz), 4.38 (ddd, 1H, $J = 2.3$Hz, $J = 5.3$Hz, $J = 6.3$Hz), 3.92 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 3.60 (m, 1H), 3.54 (qd, 1H, $J = 7.1$Hz, $J = 9.6$Hz), 2.24 (m, 1H), 1.15-1.65 (m, 13H), 0.89 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 144.6, 130.1, 127.2, 126.6 (q, $J = 272.9$Hz), 125.1 (q, $J = 3.7$Hz), 125.1, 123.9, 99.4, 77.8, 75.8, 64.9, 38.4, 31.7, 29.5, 29.5, 26.8, 22.6, 15.0, 14.0. HRMS (ESI) for C$_{21}$H$_{29}$F$_3$NaO$_3$: calcd. 409.19657; found. 409.19661.

4.5) Synthesis of (R)-((2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)(4-fluorophenyl)methanol (6cf)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2]/ allylboration using (Z)-1-ethoxyoct-1-ene 2c (62% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.38 (ddd, 2H, $J = 3.0$Hz, $J = 5.5$Hz, $J = 8.0$Hz), 7.05 (ddd, 2H, $J = 3.0$Hz, $J = 5.0$Hz, $J = 10.0$Hz), 5.80 (ddd, 1H, $J = 2.4$Hz, $J = 4.1$Hz, $J = 10.4$Hz), 5.38 (ddd, 1H, $J = 1.9$Hz, $J = 1.9$Hz, $J =
10.3Hz), 4.77 (d, 1H, J = 3.5Hz), 4.56 (d, 1H, J = 7.0Hz), 4.29 (ddd, 1H, J = 2.4Hz, J = 5.0Hz, J = 7.3Hz), 3.95 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.56 (qd, 1H, J = 7.1Hz, J = 9.7Hz), 3.43 (d, 1H, J = 2.3Hz), 2.23 (m, 1H), 1.10-1.70 (m, 13H), 0.86 (m, 3H). \( ^{13}C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \): 162.4 (d, J = 245.2Hz), 136.0 (d, J = 3.1Hz), 129.9, 128.7 (d, J = 8.1Hz), 124.0, 115.1 (d, J = 21.3Hz), 99.7, 78.3, 76.1, 64.8, 38.6, 36.6, 31.7, 29.5, 26.8, 22.6, 15.1, 14.0. HRMS (ESI) for C\(_{20}\)H\(_{29}\)FNaO\(_3\): calcd. 359.19973; found, 359.19987.

4.6) Synthesis of \((R)-1-((2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)pentan-1-ol\) (6cl)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component \([4+2]/\) allylation using \((Z)-1\)-ethoxycet-1-ene 2c (72% yield). \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 5.80 (ddd, 1H, J = 2.4Hz, J = 4.3Hz, J = 10.3Hz), 5.60 (ddd, 1H, J = 1.8Hz, J = 1.8Hz, J = 10.3Hz), 4.69 (d, 1H, J = 3.4Hz), 4.10 (ddd, 1H, J = 2.5Hz, J = 2.5Hz, J = 5.0Hz), 3.89 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.49 (m, 2H), 2.71 (m, 1H), 2.17 (m, 1H), 1.05-1.80 (m, 17H), 1.21 (dd, 3H, J = 10.0Hz, J = 17.1Hz), 0.86 (m, 6H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 129.5, 125.6, 99.6, 77.1, 73.3, 64.6, 38.7, 32.8, 31.7, 29.5, 29.4, 27.8, 26.8, 22.7, 22.5, 14.9, 14.0, 13.9. HRMS (ESI) for C\(_{18}\)H\(_{34}\)NaO\(_3\): calcd. 321.24049; found. 321.24076.

4.7) Synthesis of \((R)-cyclohexyl((2R,5R,6S)-6-ethoxy-5-hexyl-5,6-dihydro-2H-pyran-2-yl)methanol\) (6cm)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component \([4+2]/\) allylation using \((Z)-1\)-ethoxycet-1-ene 2c (43% yield). \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 5.83 (ddd, 1H, J = 2.5Hz, J = 4.2Hz, J = 10.3Hz), 5.61 (ddd, 1H, J = 1.8Hz, J = 1.8Hz, J = 10.3Hz), 4.70 (d, 1H, J = 3.5Hz), 4.37 (m, 1H), 3.90 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.51 (qd, 1H, J = 7.1Hz, J = 9.6Hz), 3.16 (ddd, 1H, J = 3.9Hz, J = 7.1Hz, J = 7.1Hz), 2.54 (d, 1H, J = 7.2Hz), 2.18
m, 1H), 1.97 (dd, 1H, J = 1.4 Hz, J = 11.6 Hz), 1.51-2.85 (m, 6H), 0.95-1.50 (m, 17H), 0.87 (m, 3H). 13C NMR (100 MHz, CDCl3) δ: 129.4, 126.4, 99.6, 77.4, 74.3, 40.3, 38.6, 31.7, 29.6, 29.5, 28.5, 26.9, 26.4, 26.2, 26.1, 26.0, 22.6, 15.0, 14.0. HRMS (ESI) for C20H36NaO3: calcd. 347.25634; found, 347.25651.

4.8) Synthesis of (S)-(2R,5R,6S)-6-Ethoxy-5,6-Dihydro-5-Methyl-2H-Pyran-2-yl)(Furan-2-yl)Methanol (6cs)

The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using (Z)-1-ethoxyoct-1-ene and cinnamylaldehyde (75% yield). 1H-NMR (400 MHz, CDCl3) δ: 7.40 (d, 1H, J = 7.0 Hz), 7.31 (dd, 1H, J = 7.7 Hz, J = 7.0 Hz), 7.24 (m, 1H), 6.73 (d, 1H, J = 15.9 Hz), 6.28 (dd, 1H, J = 6.3 Hz, J = 15.9 Hz), 5.85 (ddd, 1H, J = 2.3 Hz, J = 3.9 Hz, J = 10.4 Hz), 5.71 (ddd, 1H, J = 1.8 Hz, J = 1.9 Hz, J = 10.4 Hz), 4.78 (d, 1H, J = 3.5 Hz), 4.27 (m, 2H), 3.97 (qd, 1H, J = 7.1 Hz, J = 9.6 Hz), 3.54 (qd, 1H, J = 7.1 Hz, J = 9.6 Hz), 3.27 (bs, 1H), 2.26 (m, 1H), 1.20–1.60 (m, 10H), 0.80–0.10 (m, 6H). 13C-NMR (100 MHz, CDCl3) δ: 136.7, 132.3, 129.6, 128.4, 128.3, 127.6, 126.5, 124.7, 99.5, 74.8, 64.8, 38.5, 31.8, 31.6, 29.5, 26.9, 22.6, 15.0, 14.1, 14.0.


The title compound was prepared using the general procedure for the Cr(III)-catalyzed three-component [4+2] cycloaddition/allylboration using (Z)-1-ethoxyoct-1-ene and 2-hexenal (57% yield). 1H-NMR (400 MHz, CDCl3) δ: 5.75 (m, 2H), 5.58 (d, 1H, J = 10.4 Hz), 5.45 (dd, 1H, J = 6.8 Hz, J = 7.2 Hz), 4.70 (d, 1H, J = 3.6 Hz), 4.10 (m, 1H), 3.90 (qd, 1H, J = 7.0 Hz, J = 9.7 Hz), 3.48 (m, 1H), 3.0 (bs, 1H), 2.18 (m, 1H), 0.95-1.80 (m, 21H), 0.86 (m, 3H). 13C-NMR (100 MHz, CDCl3) δ: 134.5, 129.3, 128.5, 124.8, 99.6, 75.0, 64.5, 38.6, 34.4, 31.7, 31.5, 29.5, 29.4, 26.8, 22.5, 22.1, 14.9, 14.0, 13.5.
5) General Procedure for Acetal Reduction

To a solution of the acetal 6 (1 mmol) and triethylsilane (2 mmol) in CH₂Cl₂ (15 mL) was added BF₃·OEt₂ (2 mmol) dropwise at −50 °C. After being stirred for 2 h at −50°C, the reaction mixture was allowed to warm up to ambient temperature, after 16 h, the reaction was quenched with an aqueous saturated NaHCO₃ solution (5 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na₂SO₄, filtered, concentrated, and purified by automated flash chromatography (hexane/EtOAc 4:1) to afford the title compound.

5.1) Synthesis of (R)-((R)-5,6-dihydro-2H-pyran-2-yl)(phenyl)methanol (7aa)

The title compound was prepared using the general procedure for acetal reduction (51% yield). ¹H NMR (500 MHz, CDCl₃) δ: 7.36 (m, 5H), 5.91 (m, 1H), 5.36 (ddd, 1H, J = 2.1 Hz, J = 4.1 Hz, J = 10.4 Hz), 4.55 (d, 1H, J = 8.0 Hz), 4.15 (m, 1H), 4.04 (m, 1H), 3.74 (ddd, 1H, J = 4.3 Hz, J = 8.3 Hz, J = 11.2 Hz), 3.24 (bs, 1H), 2.25 (m, 1H), 2.04 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ: 139.8, 128.3, 128.0, 127.3, 126.7, 125.8, 78.0, 76.3, 62.6, 25.1. HRMS (ESI) for C₁₂H₁₄NaO₂: calcd. 213.08932; found, 213.08913.

5.2) Synthesis of 4-((R)-((R)-5,6-dihydro-2H-pyran-2-yl)(hydroxy)methyl) benzonitrile (7ab)

The title compound was prepared using the general procedure for acetal reduction (31% yield). ¹H NMR (500 MHz, CDCl₃) δ: 7.64 (dd, 2H, J = 1.8 Hz, J = 8.4 Hz), 7.50 (m, 2H), 5.96 (m, 1H), 5.37 (ddd, 1H, J = 2.0 Hz, J = 4.1 Hz, J = 10.4 Hz), 4.62 (dd, 1H, J = 1.9 Hz, J = 6.9 Hz), 4.12 (m, 1H), 4.00 (ddd, 1H, J = 3.7 Hz, J = 5.4 Hz, J = 11.3 Hz), 3.71 (ddd, 1H, J = 4.2 Hz, J = 8.6 Hz, J = 11.3 Hz), 3.26 (d, 1H, J = 2.6 Hz), 2.24 (m, 1H), 2.02 (m, 1H). ¹³C NMR (125
MHz, CDCl₃) δ: 145.5, 132.0, 127.9, 127.8, 125.0, 118.7, 111.6, 77.5, 75.5, 62.7, 25.0. HRMS (ESI) for C₁₃H₁₃NNaO₂: calcd. 238.08511; found, 238.08542.

5.3) Synthesis of (R)-1-((R)-5,6-dihydro-2H-pyran-2-yl)-3-phenylpropan-1-ol (7ai)

The title compound was prepared using the general procedure for acetal reduction (45% yield). ¹H NMR (500 MHz, CDCl₃) δ: 7.24 (m, 5H), 5.97 (dddd, 1H, J = 0.8Hz, J = 2.2Hz, J = 2.9Hz, J = 5.0Hz, J = 10.2Hz), 5.67 (dddd, 1H, J = 1.7Hz, J = 2.4Hz, J = 3.5Hz, J = 10.4Hz), 4.00 (m, 2H), 3.70 (dddd, 1H, J = 4.0Hz, J = 9.4Hz, J = 11.2Hz), 3.58 (dd, 1H, J = 6.0Hz, J = 11.9Hz), 2.91 (m, 1H), 2.73 (td, 1H, J = 8.2Hz, J = 13.7Hz), 2.51 (bs, 1H), 2.28 (m, 1H), 1.99 (m, 1H), 1.86 (dt, 2H, J = 6.7Hz, J = 8.4Hz). ¹³C NMR (125 MHz, CDCl₃) δ: 142.1, 128.5, 128.3, 127.0, 126.6, 125.7, 76.8, 72.5, 63.0, 34.5, 31.9, 25.2. HRMS (ESI) for C₁₄H₁₈NaO₂: calcd. 241.12038; found, 241.12053.

5.4) Synthesis of (R)-((R)-5,6-dihydro-2H-pyran-2-yl)(p-tolyl)methanol (7ac)

The title compound was prepared using the general procedure for acetal reduction (13% yield). ¹H NMR (500 MHz, CDCl₃) δ: 7.27 (d, 1H, J = 8.1Hz), 7.17 (d, 1H, J = 7.9Hz), 5.90 (m, 1H), 5.36 (dd, 1H, J = 2.0Hz, J = 4.1Hz, J = 10.4Hz), 4.52 (d, 1H, J = 8.0Hz), 4.13 (dq, 1H, J = 2.9Hz, J = 5.2Hz), 4.04 (m, 1H), 3.74 (dd, 1H, J = 4.3Hz, J = 8.3Hz, J = 11.2Hz), 3.11 (d, 1H, J = 0.5Hz), 2.35 (s, 1H), 2.25 (dd, 1H, J = 2.7Hz, J = 5.4Hz, J = 8.5Hz, J = 19.8Hz), 2.04 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ: 137.7, 136.8, 129.0, 127.2, 126.6, 125.9, 78.0, 76.2, 62.6, 25.1, 21.1. HRMS (ESI) for C₁₃H₁₆NaO₂: calcd. 227.10478; found, 227.10497.
5.5) Synthesis of (R)-((R)-5,6-dihydro-2H-pyran-2-yl)(o-tolyl)methanol (7ag)

The title compound was prepared using the general procedure for acetal reduction (57% yield). \textit{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\): 7.49 (dd, 1H, \(J = 1.4Hz, J = 7.6Hz\)), 7.24 (m, 1H), 7.19 (m, 1H), 7.14 (dd, 1H, \(J = 1.5Hz, J = 7.5Hz\)), 5.90 (m, 1H), 5.28 (ddd, 1H, \(J = 2.1Hz, J = 4.1Hz, J = 10.4Hz\)), 4.87 (d, 1H, \(J = 8.2Hz\)), 4.19 (m, 1H), 4.06 (m, 1H), 3.76 (ddd, 1H, \(J = 4.3Hz, J = 8.2Hz, J = 11.3Hz\)), 3.14 (bs, 1H), 2.35 (s, 3H), 2.27 (m, 1H), 2.05 (m, 1H). \textit{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\): 137.9, 135.7, 130.3, 127.6, 126.9, 126.8, 126.2, 125.7, 78.3, 72.0, 62.5, 25.1, 19.7. \textit{HRMS} (ESI) for C\textsubscript{13}H\textsubscript{16}NaO\textsubscript{2}: calcd. 227.10478; found, 227.10469.

5.6) Synthesis of (R)-((R)-5,6-dihydro-2H-pyran-2-yl)(4-nitrophenyl)methanol (7ad)

The title compound was prepared using the general procedure for acetal reduction (74% yield). \textit{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\): 8.21 (m, 2H), 7.57 (m, 1H), 5.98 (m, 1H), 5.40 (ddd, 1H, \(J = 1.9Hz, J = 4.2Hz, J = 10.4Hz\)), 4.69 (d, 1H, \(J = 6.8Hz\)), 4.15 (m, 1H), 4.01 (ddd, 1H, \(J = 3.7Hz, J = 5.4Hz, J = 11.3Hz\)), 3.72 (ddd, 1H, \(J = 4.2Hz, J = 8.6Hz, J = 11.3Hz\)), 3.25 (d, 1H, \(J = 2.3Hz\)), 2.25 (m, 1H), 2.03 (m, 1H). \textit{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\): 147.5, 128.0, 127.9, 125.0, 123.4, 77.5, 75.4, 62.8, 25.0. \textit{HRMS} (ESI) for C\textsubscript{12}H\textsubscript{13}NNaO\textsubscript{4}: calcd. 258.07451; found, 258.07434.

5.7) Synthesis of (R)-(4-(trifluoromethyl) phenyl) ((R)-5,6-dihydro-2H-pyran-2-yl) methanol (7ae)

The title compound was prepared using the general procedure for acetal reduction (59% yield). \textit{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.62 (d, 2H, \(J = 8.0Hz\)), 7.52 (dd, 2H, \(J = 0.6Hz, J = 8.0Hz\)), 5.96 (m, 1H), 5.38 (ddd, 1H, \(J = 2.0Hz, J = 4.1Hz, J = 10.4Hz\)), 4.63 (dd, 1H, \(J = 1.7Hz, J = 7.4Hz\)), 4.13 (m, 1H), 4.04 (m, 1H), 3.74 (ddd, 1H, \(J = 4.2Hz, J = 8.4Hz, J = 10.4Hz\)),
11.3 Hz), 3.23 (d, 1H, J = 2.3 Hz), 2.27 (m, 1H), 2.05 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 144.0, 130.1 (q, J = 32.2 Hz), 127.5, 127.4, 125.2, 125.2 (q, J = 3.8 Hz), 124.1 (q, J = 270.5 Hz), 77.7, 75.7, 62.7, 25.0. HRMS (ESI) for C$_{13}$H$_{13}$F$_3$NaO$_2$: calcd. 281.07663; found, 281.07673.

5.8) Synthesis of (R)-(4-fluorophenyl)((R)-5,6-dihydro-2H-pyran-2-yl)methanol (7af)

The title compound was prepared using the general procedure for acetal reduction (53% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.35 (m, 2H), 7.04 (m, 2H), 5.91 (m, 1H), 5.33 (ddd, 1H, J = 2.0 Hz, J = 4.1 Hz, J = 10.4 Hz), 4.53 (d, 1H, J = 7.9 Hz), 4.09 (dq, 1H, J = 2.8 Hz, J = 5.2 Hz, J = 11.2 Hz), 3.73 (ddd, 1H, J = 4.3 Hz, J = 8.4 Hz, J = 11.2 Hz), 3.26 (s, 1H), 2.24 (m, 1H), 2.03 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 163.4 (d, J = 244.5 Hz), 135.6 (d, J = 3.1 Hz), 128.9 (d, J = 8.0 Hz), 127.0, 125.4, 115.1 (d, J = 21.3 Hz), 78.0, 75.6, 62.6, 25.0. HRMS (ESI) for C$_{12}$H$_{13}$FNaO$_2$: calcd. 231.07983; found, 231.07956.

5.9) Synthesis of (R)-(2-fluorophenyl)((R)-5,6-dihydro-2H-pyran-2-yl)methanol (7ah)

The title compound was prepared using the general procedure for acetal reduction (91% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.53 (ddd, 1H, J = 1.8 Hz, J = 7.6 Hz, J = 7.6 Hz), 7.26 (ddd, 1H, J = 1.9 Hz, J = 5.3 Hz, J = 7.2 Hz, J = 8.2 Hz), 7.15 (ddd, 1H, J = 1.3 Hz, J = 7.6 Hz, J = 7.6 Hz), 7.01 (ddd, 1H, J = 1.2 Hz, J = 8.2 Hz, J = 10.4 Hz), 5.93 (m, 1H), 5.41 (ddd, 1H, J = 1.9 Hz, J = 1.9 Hz, J = 10.4 Hz), 4.94 (d, 1H, J = 7.2 Hz), 4.21 (m, 1H), 4.02 (ddd, 1H, J = 3.7 Hz, J = 5.4 Hz, J = 11.2 Hz), 3.71 (ddd, 1H, J = 4.2 Hz, J = 8.6 Hz, J = 11.2 Hz), 3.32 (m, 1H), 2.25 (m, 1H), 2.00 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 160.0 (d, J = 245.2 Hz), 129.2 (d, J = 8.2 Hz), 128.6 (d, J = 4.1 Hz), 127.3 (d, J = 12.9 Hz), 127.1, 125.6, 124.2 (d, J = 3.5 Hz), 115.1 (d, J = 21.9 Hz), 77.4 (d, J = 23.3 Hz), 69.4 (d, J = 1.6 Hz), 62.7, 25.0. HRMS (ESI) for C$_{12}$H$_{13}$FNaO$_2$: calcd. 231.07983; found, 231.07994.
5.10) Synthesis of (R)-((R)-5,6-dihydro-2H-pyran-2-yl)(naphthalen-2-yl)methanol (7aj)

The title compound was prepared using the general procedure for acetal reduction (78% yield). \( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 7.85 (m, 4H), 7.50 (m, 3H), 5.92 (m, 1H), 5.39 (m, 1H), 4.74 (d, 1H, \( J = 7.8\)Hz), 4.27 (m, 1H), 4.08 (m, 1H), 3.77 (m, 1H), 3.36 (bs, 1H), 2.28 (m, 1H), 2.05 (m, 1H). \( ^{13}\text{C NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \):137.3, 133.3, 133.2, 128.1, 128.0, 127.7, 126.8, 126.5, 126.0, 125.9, 125.8, 125.0, 78.0, 76.5, 62.6, 25.1. HRMS (ESI) for \( \text{C}_{16}\text{H}_{16}\text{NaO}_2 \); calcd. 263.10481; found, 263.10497.

5.11) Synthesis of (R)-(2-bromo-5-fluorophenyl)((R)-5,6-dihydro-2H-pyran-2-yl)methanol (7ak)

The title compound was prepared using the general procedure for acetal reduction (88% yield). \( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 7.48 (dd, 1H, \( J = 5.2\)Hz, \( J = 8.8\)Hz), 7.31 (dd, 1H, \( J = 3.1\)Hz, \( J = 9.6\)Hz), 6.89 (ddd, 1H, \( J = 3.1\)Hz, \( J = 7.7\)Hz, \( J = 8.7\)Hz), 6.01 (m, 1H), 5.54 (ddd, 1H, \( J = 1.9\)Hz, \( J = 4.0\)Hz, \( J = 10.4\)Hz), 5.01 (dd, 1H, \( J = 4.0\)Hz, \( J = 4.3\)Hz), 4.24 (m, 1H), 4.03 (ddd, 1H, \( J = 3.1\)Hz, \( J = 5.5\)Hz, \( J = 11.2\)Hz), 3.70 (ddd, 1H, \( J = 4.0\)Hz, \( J = 9.1\)Hz, \( J = 11.2\)Hz), 3.18 (d, 1H, \( J = 4.2\)Hz), 2.32 (m, 1H), 2.01 (m, 1H). \( ^{13}\text{C NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \): 162.1 (d, \( J = 246.5\)Hz), 142.0 (d, \( J = 7.1\)Hz), 133.7 (d, \( J = 7.8\)Hz), 127.6, 126.0, 116.4 (d, \( J = 20.1\)Hz), 116.2 (d, \( J = 21.4\)Hz), 76.7, 73.9, 63.2, 25.0. HRMS (ESI) for \( \text{C}_{12}\text{H}_{12}\text{BrFNaO}_2 \); calcd. 308.99041; found, 308.99037.

5.12) Synthesis of (R)-1-((R)-5,6-dihydro-2H-pyran-2-yl)pentan-1-ol (7al)

The title compound was prepared using the general procedure for acetal reduction (59% yield). \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \): 5.91 (m, 1H), 5.63 (ddd, 1H, \( J = 2.0\)Hz, \( J = 4.5\)Hz, \( J = 10.5\)Hz), 3.95 (m, 2H),
3.64 (m, 1H), 3.48 (bs, 1H), 2.48 (bs, 1H), 2.22 (m, 1H), 1.93 (m, 1H), 1.10-1.60 (m, 7H), 0.87 (t, 3H, J = 7.5Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 126.8, 126.7, 76.7, 73.1, 63.0, 32.3, 27.8, 25.2, 22.7, 13.9. HRMS (ESI) for C$_{10}$H$_{18}$NaO$_2$: calcd. 193.12039; found, 193.12053.

5.13) Synthesis of (R)-cyclohexyl][(R)-5,6-dihydro-2H-pyran-2-yl)methanol (7am)

The title compound was prepared using the general procedure for acetal reduction (73% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ: 5.94 (m, 1H), 5.62 (ddd, 1H, J = 1.8Hz, J = 4.1Hz, J = 10.4Hz), 4.13 (m, 1H), 3.97 (m, 1H), 3.64 (ddd, 1H, J = 4.0Hz, J = 9.6Hz, J = 11.2Hz), 3.20 (dd, 1H, J = 5.2Hz, J = 5.3Hz), 2.25 (m, 2H), 1.64 (m, 7H), 1.16 (m, 5H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 127.6, 126.8, 77.3, 74.0, 63.1, 39.6, 29.7, 27.9, 26.4, 26.3, 26.1, 25.2. HRMS (ESI) for C$_{12}$H$_{20}$NaO$_2$: calcd. 219.13662; found, 219.13686.

5.14) Synthesis of (R)-([2R,5R]-5,6-dihydro-5-methyl-2H-pyran-2-yl)(phenyl) methanol (7ba)

The title compound was prepared using the general procedure for acetal reduction (52% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.34 (m, 5H), 5.81 (ddd, 1H, J = 2.3Hz, J = 3.9Hz, J = 10.4Hz), 5.29 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.4Hz), 4.56 (d, 1H, J = 8.3Hz), 4.10 (qd, 1H, J = 2.4Hz, J = 8.1Hz), 3.81 (dd, 1H, J = 4.4Hz, J = 11.1Hz), 3.61 (dd, 1H, J = 5.0Hz, J = 11.1Hz), 3.24 (bs, 1H), 2.26 (m, 1H), 1.05 (d, 3H, J = 7.1Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 139.8, 132.842, 128.3, 128.0, 127.3, 124.5, 77.9, 76.8, 68.0, 29.3, 17.8. HRMS (ESI) for C$_{13}$H$_{29}$NaO$_2$: calcd. 227.10483; found, 227.10491.


The title compound was prepared using the general procedure for acetal reduction (48% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.20 (bs, 1H), 7.35 (m, 5H), 5.81 (ddd, 1H, J = 2.3Hz, J = 3.9Hz, J = 10.4Hz), 5.29 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.4Hz), 4.56 (d, 1H, J = 8.3Hz), 4.10 (qd, 1H, J = 2.4Hz, J = 8.1Hz), 3.81 (dd, 1H, J = 4.4Hz, J = 11.1Hz), 3.61 (dd, 1H, J = 5.0Hz, J = 11.1Hz), 3.24 (bs, 1H), 2.26 (m, 1H), 1.05 (d, 3H, J = 7.1Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 139.8, 132.842, 128.3, 128.0, 127.3, 124.5, 77.9, 76.8, 68.0, 29.3, 17.8. HRMS (ESI) for C$_{13}$H$_{29}$NaO$_2$: calcd. 227.10483; found, 227.10491.
MHz, CDCl$_3$) $\delta$: 7.64 (dd, 2H, $J = 1.8$Hz, $J = 8.4$Hz), 7.50 (m, 2H), 5.86 (ddd, 1H, $J = 2.1$Hz, $J = 3.9$Hz, $J = 10.4$Hz), 5.30 (ddd, 1H, $J = 2.0$Hz, $J = 2.0$Hz, $J = 10.5$Hz), 4.63 (d, 1H, $J = 7.4$Hz), 4.06 (m, 1H), 3.79 (dd, 1H, $J = 4.3$Hz, $J = 11.1$Hz), 3.58 (dd, 1H, $J = 4.7$Hz, $J = 11.1$Hz), 3.26 (bs, 1H), 2.24 (m, 1H), 1.02 (d, 3H, $J = 7.1$Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 145.4, 133.7, 132.0, 127.9, 123.6, 118.7, 111.7, 77.5, 75.3, 68.2, 29.3, 17.8.

HRMS (ESI) for C$_{14}$H$_{15}$NNaO$_2$: calcd. 252.0995; found, 252.0997.

5.16) Synthesis of (R)-1-((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)-3-phenyl propan-1-ol (7bi)

The title compound was prepared using the general procedure for acetal reduction (52% yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.24 (m, 5H), 5.89 (ddd, 1H, $J = 2.3$Hz, $J = 4.3$Hz, $J = 10.4$Hz), 5.63 (ddd, 1H, $J = 1.9$Hz, $J = 10.4$Hz), 3.94 (ddd, 1H, $J = 2.3$Hz, $J = 4.7$Hz, $J = 6.7$Hz), 3.78 (ddd, 1H, $J = 4.2$Hz, $J = 11.1$Hz), 3.68 (m, 1H), 3.60 (dd, 2H, $J = 3.8$Hz, $J = 11.1$Hz), 2.91 (ddd, 1H, $J = 6.3$Hz, $J = 9.1$Hz, $J = 13.9$Hz), 2.73 (ddd, 1H, $J = 7.3$Hz, $J = 9.3$Hz, $J = 13.8$Hz), 2.21 (m, 1H), 1.85 (m, 2H), 1.06 (d, 3H, $J = 7.1$Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 142.1, 132.9, 128.5, 128.3, 125.7, 125.2, 76.8, 72.3, 68.5, 34.5, 31.9, 29.5, 18.2. HRMS (ESI) for C$_{15}$H$_{20}$NaO$_2$: calcd. 255.1355; found, 255.1357.

5.17) Synthesis of (R)-((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)(o-tolyl)methanol (7bg)

The title compound was prepared using the general procedure for acetal reduction (31% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.50 (m, 1H), 7.19 (m, 3H), 5.80 (ddd, 1H, $J = 2.3$Hz, $J = 3.7$Hz, $J = 10.4$Hz), 5.22 (ddd, 1H, $J = 2.0$Hz, $J = 2.0$Hz, $J = 10.4$Hz), 4.90 (d, 1H, $J = 8.3$Hz), 4.15 (m, 1H), 3.83 (dd, 1H, $J = 4.5$Hz, $J = 11.1$Hz), 3.62 (dd, 1H, $J = 5.1$Hz, $J = 11.1$Hz), 3.05 (bs, 1H), 2.35 (s, 3H), 2.26 (bs, 1H), 1.06 (d, 3H, $J = 7.1$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 138.2, 135.9, 133.2, 130.5, 127.9, 127.1, 126.4, 124.7, 78.5, 71.9, 68.2, 29.6, 19.9, 18.109. HRMS (ESI) for C$_{14}$H$_{18}$NaO$_2$: calcd. 241.12048; found, 241.12053.

R. M. Al-Zoubi, and D. G. Hall
5.18) Synthesis of (R)-(4-(trifluoromethyl)phenyl)((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (7be)

The title compound was prepared using the general procedure for acetal reduction (61% yield). ^1H NMR (500 MHz, CDCl₃) δ: 7.61 (d, 2H, J = 8.5Hz), 7.50 (d, 2H, J = 8.0Hz), 5.85 (ddd, 1H, J = 2.2Hz, J = 3.9Hz, J = 10.4Hz), 5.28 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.4Hz), 4.63 (d, 1H, J = 7.8Hz), 4.08 (m, 1H), 4.01 (bs, 1H), 3.80 (dd, 1H, J = 4.4Hz, J = 11.1Hz), 3.59 (dd, 1H, J = 4.9Hz, J = 11.1Hz), 2.25 (m, 1H), 1.04 (d, 3H, J = 7.1Hz).

^13C NMR (125 MHz, CDCl₃) δ: 143.8, 133.5, 130.2 (q, J = 32.3Hz), 127.6, 126.2 (q, J = 271.6Hz), 125.2 (q, J = 3.6Hz), 123.8, 77.6, 75.5, 68.0, 29.3, 17.7. HRMS (ESI) for C₁₄H₁₅F₃NaO₂: calcd. 295.09164; found, 295.09243.

5.19) Synthesis of (R)-(4-fluorophenyl)((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (7bf)

The title compound was prepared using the general procedure for acetal reduction (60% yield). ^1H NMR (500 MHz, CDCl₃) δ: 7.36 (m, 2H), 7.05 (m, 2H), 5.82 (ddd, 1H, J = 2.2Hz, J = 3.9Hz, J = 10.4Hz), 5.27 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.4Hz), 4.55 (dd, 1H, J = 1.7Hz, J = 8.2Hz), 4.05 (m, 1H), 3.81 (dd, 1H, J = 4.4Hz, J = 11.1Hz), 3.60 (dd, 1H, J = 4.9Hz, J = 11.1Hz), 3.19 (d, 1H, J = 1.7Hz), 2.26 (m, 1H), 1.05 (d, 3H, J = 7.1Hz). ^13C NMR (125 MHz, CDCl₃) δ: 162.5 (d, J = 245.5Hz), 135.5 (d, J = 3.1Hz), 133.1, 128.9 (d, J = 8.0Hz), 124.1, 115.2 (d, J = 21.4Hz), 77.9, 75.4, 68.0, 29.3, 17.8. HRMS (ESI) for C₁₄H₁₅FNaO₂: calcd. 245.09544; found, 245.09587.

5.20) Synthesis of (R)-(2-fluorophenyl)((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (7bh)

The title compound was prepared using the general procedure for acetal reduction (69% yield). ^1H NMR (400 MHz, CDCl₃) δ: 7.54 (ddd, H, J = 1.9Hz, J = 7.4Hz, J = 7.4Hz), 7.27 (m, 1H),
7.17 (ddd, 1H, J = 1.2Hz, J = 7.5Hz, J = 7.5Hz), 7.03 (ddd, 1H, J = 1.2Hz, J = 8.2Hz, J = 10.2Hz), 5.85 (ddd, 1H, J = 2.3Hz, J = 3.9Hz, J = 10.4Hz), 5.35 (ddd, 1H, J = 1.8Hz, J = 3.6Hz, J = 10.4Hz), 4.96 (d, 1H, J = 7.6Hz), 4.17 (ddd, 1H, J = 4.7Hz, J = 7.5Hz), 3.81 (ddd, 1H, J = 4.4Hz, J = 11.1Hz), 3.62 (ddd, 1H, J = 4.7Hz, J = 11.1Hz), 3.20 (bs, 1H), 2.25 (m, 1H), 1.06 (d, 1H, J = 2.45Hz), 0.90 (t, 3H, J = 7.2Hz).

5.21) Synthesis of (R)-(2-bromo-5-fluorophenyl)((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)methanol (7bk)

The title compound was prepared using the general procedure for acetal reduction (76% yield). 1H NMR (500 MHz, CDCl3) δ: 7.49 (dd, 1H, J = 5.2Hz, J = 8.8Hz), 7.32 (dd, 1H, J = 3.1Hz, J = 9.6Hz), 6.89 (dd, 1H, J = 3.1Hz, J = 7.7Hz, J = 8.7Hz), 5.92 (dd, 1H, J = 2.2Hz, J = 4.1Hz, J = 10.3Hz), 5.45 (ddd, 1H, J = 1.9Hz, J = 10.3Hz, J = 10.3Hz), 5.04 (m, 1H), 4.17 (m, 1H), 3.80 (dd, 1H, J = 4.3Hz, J = 11.1Hz), 3.64 (ddd, 1H, J = 4.2Hz, J = 11.1Hz), 3.13 (d, 1H, J = 3.7Hz), 2.24 (m, 1H), 1.09 (d, 3H, J = 7.1Hz).

13C NMR (125 MHz, CDCl3) δ: 162.1 (d, J = 246.5Hz), 141.8 (d, J = 6.8Hz), 133.7 (d, J = 8.0Hz), 133.5, 124.5, 116.6 (d, J = 3.0Hz), 116.4 (d, J = 22.4Hz), 116.1 (d, J = 23.6Hz), 77.0, 73.6, 68.5, 29.2, 18.1. HRMS (ESI) for C13H15FNaO2: calcd. 323.00592; found, 323.00584.

5.22) Synthesis of (R)-1-((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl)pentan-1-ol (7bl)

The title compound was prepared using the general procedure for acetal reduction (76% yield). 1H NMR (500 MHz, CDCl3) δ: 5.87 (ddd, 1H, J = 2.3Hz, J = 4.2Hz, J = 10.4Hz), 5.62 (ddd, 1H, J = 1.9Hz, J = 19Hz, J = 10.4Hz), 3.88 (ddd, 1H, J = 2.3Hz, J = 4.6Hz, J = 6.7Hz), 3.75 (dd, 1H, J = 4.2Hz, J = 11.1Hz), 3.57 (dd, 1H, J = 4.0Hz, J = 11.1Hz), 3.53 (m, 1H), 2.45 (dd, 1H, J = 0.6Hz, J = 1.0Hz), 2.20 (m, 1H), 1.30-1.60 (m, 6H), 1.03 (d, 3H, J = 7.1Hz), 0.90 (t, 3H, J = 7.2Hz). 

13C NMR (125 MHz, CDCl3) δ: 132.7, 125.4, 76.8, 72.9,
68.4, 65.8, 32.3, 29.5, 27.8, 22.7, 18.2, 15.2, 14.0. **HRMS** (ESI) for C_{11}H_{20}NaO_{2}: calcd. 207.13629; found, 207.13654.

5.23) Synthesis of (R)-cyclohexyl((2R,5R)-5,6-dihydro-5-methyl-2H-pyran-2-yl) methanol (7bm)

The title compound was prepared using the general procedure for acetal reduction (81% yield). **1H NMR** (500 MHz, CDCl3) δ: 5.87 (ddd, 1H, J = 2.3Hz, J = 4.4Hz, J = 10.3Hz), 5.59 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.5Hz), 4.08 (m, 1H), 3.73 (dd, 1H, J = 4.2Hz, J = 11.1Hz), 3.75 (dd, 1H, J = 3.6Hz, J = 11.1Hz), 3.24 (dd, 1H, J = 5.5Hz, J = 5.5Hz), 2.37 (m, 1H), 2.16 (m, 2H), 1.45-1.90 (m, 10H), 1.03 (d, 3H, J = 7.1Hz). **13C NMR** (125 MHz, CDCl3) δ: 132.7, 126.1, 76.9, 74.0, 68.5, 39.6, 29.9, 29.4, 27.5, 26.4, 26.4, 26.1, 18.3. **HRMS** (ESI) for C_{11}H_{20}NaO_{2}: calcd. 233.15183; found, 233.15165.

5.24) Synthesis of (R)-((2R,5R)-5-hexyl-5,6-dihydro-2H-pyran-2-yl)(phenyl)methanol (7ca)

The title compound was prepared using the general procedure for acetal reduction (75% yield). **1H NMR** (400 MHz, CDCl3) δ: 7.32 (m, 5H), 5.83 (ddd, 1H, J = 2.2Hz, J = 4.1Hz, J = 10.5Hz), 5.29 (ddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 10.5Hz), 4.53 (d, 1H, J = 8.1Hz), 4.10 (ddd, 1H, J = 2.3Hz, J = 4.8Hz, J = 8.2Hz), 3.77 (dd, 1H, J = 4.3Hz, J = 11.2Hz), 3.70 (dd, 1H, J = 4.4Hz, J = 11.2Hz), 3.37 (bs. 1H), 2.05 (m, 1H), 1.32 (m, 10H), 0.88 (m, 3H). **13C NMR** (100 MHz, CDCl3) δ: 139.8, 131.5, 128.2, 127.9, 127.3, 124.8, 78.2, 76.2, 66.6, 34.4, 32.9, 31.7, 29.4, 27.0, 22.6, 14.0. **HRMS** (ESI) for C_{18}H_{26}NaO_{2}: calcd. 297.18327; found, 297.18343.
5.25) Synthesis of 4-((R)-((2R,5R)-5-hexyl-5,6-dihydro-2H-pyran-2-yl)(hydroxy)methyl) benzonitrile (7cb)

The title compound was prepared using the general procedure for acetal reduction (67% yield). \(^1\H NMR\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, 2H, \(J = 8.5\)Hz), 7.49 (d, 2H, \(J = 8.1\)Hz), 5.90 (ddd, 1H, \(J = 2.1\)Hz, \(J = 4.3\)Hz, \(J = 10.5\)Hz), 5.33 (ddd, 1H, \(J = 10.4\)Hz, \(J = 2\)Hz, \(J = 2\)Hz), 4.61 (dd, 1H, \(J = 2.4\)Hz, \(J = 7.2\)Hz), 4.07 (ddd, 1H, \(J = 2.3\)Hz, \(J = 4.7\)Hz, \(J = 7.1\)Hz), 3.75 (dd, 1H, \(J = 4.2\)Hz, \(J = 11.2\)Hz), 3.68 (dd, 1H, \(J = 4.0\)Hz, \(J = 11.2\)Hz), 3.28 (d, 1H, \(J = 2.3\)Hz), 2.03 (m, 1H), 1.10-1.45 (m, 10H), 0.88 (m, 3H). \(^{13}\C NMR\) (100 MHz, CDCl\(_3\)) \(\delta\): 145.4, 132.5, 131.9, 127.9, 124.0, 118.7, 111.6, 77.7, 75.4, 66.8, 34.3, 32.9, 31.7, 31.5, 29.3, 26.9, 22.5, 14.0, 14.0. \(HRMS\) (ESI) for C\(_{19}\)H\(_{25}\)N\(_2\)O\(_2\): calcd. 322.17842; found, 322.17865.

5.26) Synthesis of (R)-1-((2R,5R)-5-hexyl-5,6-dihydro-2H-pyran-2-yl)-3-phenylpropan-1-ol (7ci)

The title compound was prepared using the general procedure for acetal reduction (77% yield). \(^1\H NMR\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.25 (m, 5H), 5.95 (ddd, 1H, \(J = 2.2\)Hz, \(J = 4.5\)Hz, \(J = 10.4\)Hz), 5.65 (ddd, 1H, \(J = 1.8\)Hz, \(J = 1.8\)Hz, \(J = 10.4\)Hz), 3.95 (m, 1H), 3.74 (m, 2H), 3.59 (m, 1H), 2.92 (m, 1H), 2.74 (td, 1H, \(J = 8.1\)Hz, \(J = 13.8\)Hz), 2.57 (d, 1H, \(J = 4.0\)Hz), 2.04 (m, 1H), 1.85 (m, 2H), 1.15-1.66 (m, 10H), 0.92 (t, 3H, \(J = 6.8\)Hz). \(^{13}\C NMR\) (100 MHz, CDCl\(_3\)) \(\delta\): 142.2, 131.7, 128.5, 128.3, 125.7, 125.6, 77.1, 72.4, 67.0, 34.6, 34.5, 33.2, 31.9, 31.8, 29.4, 27.1, 22.6, 14.1. \(HRMS\) (ESI) for C\(_{20}\)H\(_{30}\)NaO\(_2\): calcd. 325.21443; found, 325.21479.
5.27) Synthesis of (R)-(4-(trifluoromethyl)phenyl)((2R,5R)-5-hexyl-5,6-dihydro-2H-pyran-2-yl)methanol (7ce)

The title compound was prepared using the general procedure for acetal reduction (71% yield). $^1$H NMR (100 MHz, CDCl$_3$) $\delta$: 7.61 (d, 1H, $J$ = 8.4Hz), 7.50 (d, 1H, $J$ = 8.1Hz), 5.90 (ddd, 1H, $J$ = 2.2Hz, $J$ = 4.2Hz, $J$ = 10.5Hz), 5.33 (ddd, 1H, $J$ = 1.6Hz, $J$ = 1.6Hz, $J$ = 10.4Hz), 4.61 (dd, 1H, $J$ = 1.8Hz, $J$ = 7.6Hz), 4.10 (m, 1H), 3.77 (dd, 1H, $J$ = 4.3Hz, $J$ = 11.2Hz), 3.71 (dd, 1H, $J$ = 4.2Hz, $J$ = 11.2Hz), 3.37 (d, 1H, $J$ = 1.9Hz), 2.07 (m, 1H), 1.10-1.50 (m, 10H), 0.89 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 144.0, 132.1 (q, $J$ = 32 Hz), 127.6, 125.1 (q, $J$ = 3.8Hz), 124.6 (q, $J$ = 268Hz), 124.2, 77.9, 75.6, 66.7, 34.4, 32.9, 31.7, 29.4, 27.0, 22.6, 14.0. HRMS (ESI) for C$_{19}$H$_{25}$F$_3$NaO$_3$: calcd. 365.17052; found, 365.17041.

5.28) Synthesis of (R)-(4-fluorophenyl)((2R,5R)-5-hexyl-5,6-dihydro-2H-pyran-2-yl) methanol (7cf)

The title compound was prepared using the general procedure for acetal reduction (51% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.34 (m, 2H), 7.03 (m, 2H), 5.86 (ddd, 1H, $J$ = 2.2Hz, $J$ = 4.2Hz, $J$ = 10.5Hz), 5.29 (ddd, 1H, $J$ = 1.9Hz, $J$ = 1.9Hz, $J$ = 10.5Hz), 4.52 (dd, 1H, $J$ = 1.6Hz, $J$ = 8.0Hz), 4.06 (ddd, 1H, $J$ = 2.3Hz, $J$ = 4.7Hz, $J$ = 8.0Hz), 3.77 (dd, 1H, $J$ = 4.3Hz, $J$ = 11.2Hz), 3.70 (dd, 1H, $J$ = 4.3Hz, $J$ = 11.2Hz), 3.28 (d, 1H, $J$ = 1.9Hz), 2.06 (m, 1H), 1.41 (m, 1H), 1.10-1.40 (m, 10H), 0.87 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 162.4 (d, $J$ = 244.7Hz), 135.6 (d, $J$ = 3Hz), 131.8, 128.9 (d, $J$ = 8.1Hz), 124.5, 115.1 (d, $J$ = 21.3Hz), 78.1, 75.5, 66.6, 34.4, 32.9, 31.7, 29.4, 27.0, 22.6, 14.0. HRMS (ESI) for C$_{18}$H$_{25}$FNaO$_2$: calcd. 315.17368; found, 315.17384.
5.29) Synthesis of \((R)-(2R,5R)-5\text{-hexyl-5,6-dihydro-2H-pyran-2-yl})\text{pentan-1-ol (7cl)}

The title compound was prepared using the general procedure for acetal reduction (97\% yield).

\(^1\)H NMR \((400\text{ MHz, CDCl}_3\) \(\delta: 5.90\text{ (ddde, 1H, } J = 0.8\text{Hz, } J = 2.2\text{Hz, } J = 4.4\text{Hz, } J = 10.4\text{Hz}), 5.62\text{ (m, 1H), 3.87 (ddd, 1H, } J = 2.2\text{Hz, } J = 4.8\text{Hz, } J = 6.2\text{Hz), 3.70 (m, 2H), 3.49 (m, 1H), 2.51 (d, 1H, } J = 3.7\text{Hz), 2.00 (m, 1H), 1.10-1.70 (m, 17H), 0.83 (m, 6H). \(^{13}\)C NMR \((100\text{ MHz, CDCl}_3\) \(\delta: 131.5, 125.7, 77.0, 73.0, 66.8, 34.6, 33.1, 32.3, 31.7, 29.3, 27.7, 27.0, 22.7, 22.5, 14.0, 13.9. HRMS (ESI) for C\(_{16}\)H\(_{30}\)NaO\(_2\): calcd. 277.21438; found, 277.21475.

5.30) Synthesis of \((R)\text{-cyclohexyl}(2R,5R)-5\text{-hexyl-5,6-dihydro-2H-pyran-2-yl})\text{methanol (7cm)}

The title compound was prepared using the general procedure for acetal reduction (67\% yield). \(^1\)H NMR \((400\text{ MHz, CDCl}_3\) \(\delta: 5.94\text{ (ddde, 1H, } J = 2.2\text{Hz, } J = 4.5\text{Hz, } J = 10.4\text{Hz}), 5.62\text{ (m, 1H), 4.11 (m, 1H), 3.72 (d, 1H, } J = 3.7\text{Hz), 3.23 (m, 1H, } J = 5.4\text{Hz), 2.19 (d, 1H, } J = 5.0\text{Hz), 1.98 (m, 1H), 1.46-1.89 (m, 6H), 1.00-1.45 (m, 16H), 0.88-0.95 (m, 3H). \(^{13}\)C NMR \((100\text{ MHz, CDCl}_3\) \(\delta: 131.5, 126.5, 77.1, 74.2, 67.0, 39.6, 34.6, 33.3, 31.7, 29.8, 29.4, 27.6, 27.1, 26.4, 26.1, 22.6, 14.0. HRMS (ESI) for C\(_{18}\)H\(_{32}\)NaO\(_2\): calcd. 303.23012; found, 303.23046.

6) General Procedure for Dihydroxylation

Dehydropyran 7 (1 mmol) was dissolved in acetone/water (10 mL, 9:1). Then, the monohydrate of \(N\)-methylmorpholine \(N\)-oxide (1.5 mmol) and osmium tetroxide (2.5 wt\% solution in 2-methyl-2-propanol) were added and the mixture was stirred at ambient temperature...
overnight. It was then diluted with aqueous sodium sulfite (5 mL) and extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na₂SO₄, filtered, concentrated, and purified by automated flash chromatography (hexane/EtOAc, 1:1) to afford the title compound as a white solid.

6.1) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(phenyl)methyl)-2H-pyran-3,4-diol (8aa)

The title compound was prepared using the general procedure for dihydroxylation (66% yield) as a white solid. [α]²³D -18.12 (c = 0.33, MeOH). IR (Cast film, cm⁻¹) 3396.5, 3061.6, 2975.6, 2875.2, 1603.2, 1452.3, 1398.7, 1266.3, 1107.9, 1079.5, 1062.1, 1039.8, 1003.2, 925.8, 717.7. ¹H NMR (400 MHz, CDCl₃) δ: 7.41 (m, 2H), 7.28 (m, 2H), 7.20 (m, 1H), 4.98 (d, 1H, J = 1.0Hz), 4.09 (dd, 1H, J = 2.9Hz, J = 6.5Hz), 3.73 (dd, 1H, J = 3.1Hz, J = 9.5Hz), 3.66 (dd, 1H, J = 1.8Hz, J = 9.6Hz), 3.60 (m, 1H), 1.84 (m, 1H), 1.71 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 143.3, 127.6, 126.6, 126.3, 78.8, 70.9, 67.9, 67.3, 61.5, 32.3. HRMS (ESI) for C₁₂H₁₆NaO₄: calcd. 247.09408; found. 247.09392.

6.2) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(p-cyanophenyl)methyl)-2H-pyran-3,4-diol (8ab)

The title compound was prepared using the general procedure for dihydroxylation (75% yield) as a white solid. [α]²³D -15.38 (c = 0.29, MeOH). IR (Cast film, cm⁻¹) 3426.1, 2927.6, 2877.2, 2229.6, 1609.1, 1463.3, 1412.0, 1268.0, 1203.8, 1108.0, 1072.4, 1040.3, 881.3. ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (dd, 1H, J = 1.6Hz, J = 8.1Hz), 7.58 (dd, 1H, J = 1.5Hz, J = 8.1Hz), 5.04 (bs, 1H), 4.10 (m, 1H), 3.75 (dd, 1H, J = 3.1Hz, J = 9.7Hz), 3.66 (dd, 1H, J = 1.7Hz, J = 9.7Hz), 3.56 (m, 2H), 3.30 (m, 1H), 1.85 (m, 1H), 1.71 (dddd, 1H, J = 2.0Hz, J = 2.0Hz, J = 3.7Hz, J = 14.1Hz). ¹³C NMR (100 MHz, CDCl₃) δ: 149.6, 131.5, 127.3, 118.7, 110.2, 78.6, 70.5, 67.7, 67.2, 61.6, 32.4. HRMS (ESI) for C₁₃H₁₃NNaO₄: calcd. 272.08933; found. 272.08971.
6.3) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-1-hydroxy-3-phenylpropyl)-2H-pyran-3,4-diol (8ai)

The title compound was prepared using the general procedure for dihydroxylation (78% yield) as a white solid. \([\alpha]^{23}_{D} -2.64 \text{ (c = 0.22, MeOH). IR (Cast film, cm}^{-1}) 3486.1, 3377.5, 3280.1, 2946.9, 2920.8, 2879.2, 1603.0, 1496.2, 1454.1, 1401.8, 1278.1, 1080.5, 1054.0, 1019.6, 913.9, 735.0. \)\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.19\) (m, 5H), 4.06 (m, 1H), 3.83 (ddd, 1H, \(J = 1.4\)Hz, \(J = 4.7\)Hz, \(J = 8.9\)Hz), 3.75 (dd, 1H, \(J = 2.3\)Hz, \(J = 11.4\)Hz), 3.69 (dd, 1H, \(J = 1.7\)Hz, \(J = 9.1\)Hz), 3.66 (dd, 1H, \(J = 3.1\)Hz, \(J = 9.7\)Hz), 3.41 (dd, 1H, \(J = 1.6\)Hz, \(J = 9.8\)Hz), 3.30 (m, 1H), 2.78 (m, 1H), 2.63 (dd, 1H, \(J = 6.9\)Hz, \(J = 9.7\)Hz, \(J = 13.6\)Hz), 1.94 (ddd, 2H, \(J = 4.8\)Hz, \(J = 9.1\)Hz, \(J = 18.8\)Hz), 1.79 (m, 2H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta: 142.5, 128.2, 128.1, 125.4, 76.9, 68.5, 67.6, 67.3, 61.5, 35.6, 32.5, 32.2. HRMS (ESI) for C\(_{14}\)H\(_{20}\)NaO\(_4\): calcd. 275.12538; found. 275.12541.

6.4) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(p-tolyl)methyl)-2H-pyran-3,4-diol (8ac)

The title compound was prepared using the general procedure for dihydroxylation (51% yield) as a white solid. \([\alpha]^{23}_{D} -10.61 \text{ (c = 0.13, MeOH). IR (Cast film, cm}^{-1}) 3391.04, 2924.9, 2875.0, 1662.5, 1604.9, 1515.3, 1412.7, 1266.3, 1107.6, 1072.3, 1038.7, 767.7. \)\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.28\) (d, 2H, \(J = 8.0\)Hz), 7.11 (d, 2H, \(J = 7.8\)Hz), 4.93 (dd, 1H, \(J = 0.5\)Hz, \(J = 1.0\)Hz), 4.08 (dd, 1H, \(J = 3.0\)Hz, \(J = 6.6\)Hz), 3.70 (dd, 1H, \(J = 3.1\)Hz, \(J = 9.6\)Hz), 3.60 (m, 2H), 3.30 (m, 1H), 2.31 (s, 3H), 1.84 (m, 1H), 1.71 (m, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta: 140.1, 136.2, 128.2, 126.3, 78.8, 70.7, 67.9, 67.2, 61.5, 32.3, 19.9. HRMS (ESI) for C\(_{13}\)H\(_{18}\)NaO\(_4\): calcd. 261.10973; found. 261.11009.
6.5) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(o-tolyl)methyl)-2H-pyran-3,4-diol (8ag)

The title compound was prepared using the general procedure for dihydroxylation (72% yield) as a white solid. [$\alpha$]$^{23}_{D}$ -42.75 (c = 0.53, MeOH). IR (Cast film, cm$^{-1}$) 3403.0, 3059.7, 3026.6, 2926.2, 2877.6, 1711.2, 1605.2, 1488.8, 1404.4, 1266.6, 1218.1, 1105.9, 1065.3, 1037.8, 769.6, 736.5. $^1$H NMR (400 MHz, CDCl$^3$) δ: 7.53 (m, 1H), 7.12 (m, 3H), 5.27 (d, 1H, $J$ = 1.5Hz), 4.10 (m, 1H), 3.77 (dd, 1H, $J$ = 3.2Hz, $J$ = 9.6Hz), 3.60 (dd, 1H, $J$ = 2.2Hz, $J$ = 7.8Hz), 3.57 (m, 2H), 3.30 (m, 1H), 2.33 (s, 3H), 1.87 (dddd, 1H, $J$ = 7.5Hz, $J$ = 10.0Hz, $J$ = 14.0Hz), 1.72 (dddd, 1H, $J$ = 2.1Hz, $J$ = 4.0Hz, $J$ = 7.6Hz, $J$ = 14.1Hz). $^{13}$C NMR (100 MHz, CDCl$^3$) δ: 141.0, 134.2, 129.7, 127.2, 126.5, 125.1, 77.2, 67.9, 67.3, 67.1, 61.5, 32.4, 18.2. HRMS (ESI) for C$_{13}$H$_{18}$NaO$_4$: calcd. 261.10973; found. 261.11044.

6.6) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-hydroxy(4-nitrophenyl)methyl)-2H-pyran-3,4-diol (8ad)

The title compound was prepared using the general procedure for dihydroxylation (85% yield) as a white solid. [$\alpha$]$^{23}_{D}$ -11.85 (c = 0.14, MeOH). IR (Cast film, cm$^{-1}$) 3404.1, 3078.9, 2927.8, 2877.5, 1604.2, 1519.0, 1349.7, 1107.3, 1072.0, 1040.3, 1003.3, 882.8, 763.2. $^1$H NMR (400 MHz, CDCl$^3$) δ: 8.18 (m, 2H), 7.63 (m, 2H), 5.10 (bs, 1H), 4.11 (dd, 1H, $J$ = 2.9Hz, $J$ = 5.8Hz), 3.76 (dd, 1H, $J$ = 3.1Hz, $J$ = 9.7Hz), 3.68 (dd, 1H, $J$ = 1.6Hz, $J$ = 9.7Hz), 3.56 (m, 2H), 1.86 (m, 1H), 1.71 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$^3$) δ: 151.6, 147.1, 127.3, 122.6, 78.6, 70.4, 67.7, 67.2, 61.7, 32.4. HRMS (ESI) for C$_{12}$H$_{15}$NNaO$_6$: calcd.292.07916; found. 292.07964.
6.7) Synthesis of (2S,3R,4R)-2-((R)-(4-(trifluoromethyl)phenyl)(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8ae)

The title compound was prepared using the general procedure for dihydroxylation (52% yield) as a white solid. \([\alpha]^{23b}_{	ext{D}} = -33.38\) (c = 0.13, MeOH). IR (Cast film, cm\(^{-1}\)) 3398.2, 2927.5, 2874.4, 1719.2, 1619.9, 1511.3, 1327.5, 1122.3, 1069.0, 1039.9, 1017.7, 1004.8, 882.5. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.59 (m, 4H), 5.05 (bs, 1H), 4.10 (m, 1H), 3.75 (dd, 1H, \(J = 3.1\)Hz, \(J = 9.7\)Hz), 3.67 (dd, 1H, \(J = 1.7\)Hz, \(J = 9.7\)Hz), 3.59 (m, 1H), 3.30 (m, 1H), 1.84 (m, 1H), 1.71 (m, 1H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 148.2 (q, \(J = 7.8\)Hz), 127.3 (q, \(J = 268.9\)Hz), 124.4 (q, \(J = 3.9\)Hz), 114.1 (q, \(J = 21.2\)Hz), 78.7, 70.5, 67.8, 67.2, 61.6, 32.4. HRMS (ESI) for C\(_{13}\)H\(_{15}\)F\(_3\)NaO\(_4\): calcd. 315.08146; found. 315.08255.

6.8) Synthesis of (2S,3R,4R)-2-((R)-(4-fluorophenyl)(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8af)

The title compound was prepared using the general procedure for dihydroxylation (86% yield) as a white solid. \([\alpha]^{23b}_{	ext{D}} = -24.26\) (c = 0.23, MeOH). IR (Cast film, cm\(^{-1}\)) 3541.8, 3440.1, 3344.8, 3057.6, 2960.0, 2923.4, 2890.8, 1602.3, 1510.8, 1421.7, 1302.0, 1214.9, 1112.6, 1046.3, 859.3. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.51 (m, 2H), 7.01 (ddd, 2H, \(J = 2.5\)Hz, \(J = 5.9\)Hz, \(J = 8.9\)Hz), 4.97 (bs, 1H), 4.09 (m, 1H), 3.72 (dd, 1H, \(J = 3.1\)Hz, \(J = 9.6\)Hz), 3.61 (m, 4H), 1.84 (ddddd, 1H, \(J = 2.6\)Hz, \(J = 7.4\)Hz, \(J = 10.3\)Hz, \(J = 12.8\)Hz), 1.71 (dddd, 1H, \(J = 2.1\)Hz, \(J = 7.5\)Hz, \(J = 3.9\)Hz, \(J = 14.1\)Hz). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 162.1 (d, \(J = 241.1\)Hz), 139.3 (d, \(J = 3.1\)Hz), 128.2 (d, \(J = 7.8\)Hz), 114.1 (d, \(J = 21.2\)Hz), 78.7, 70.3, 67.8, 67.2, 61.5, 32.3. HRMS (ESI) for C\(_{12}\)H\(_{13}\)FNaO\(_3\): calcd.265.08466; found. 265.08506.
6.9) Synthesis of (2$S$,3$R$,4$R$)-2-((R)-(2-fluorophenyl)(hydroxy)methyl)-tetrahydro-2$H$-pyran-3,4-diol (8ah)

The title compound was prepared using the general procedure for dihydroxylation (71% yield) as a white solid. $[\alpha]_{D}^{23}$ -28.62 (c = 0.32, MeOH). IR (Cast film, cm$^{-1}$) 3404.4, 3067.0, 2982.9, 2878.5, 1616.6, 1488.5, 1456.9, 1403.7, 1267.5, 1222.4, 1105.7, 1069.4, 1038.6, 1002.7, 921.8, 793.3. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.60 (ddd, 1H, $J$ = 1.1 Hz, $J$ = 7.6 Hz, $J$ = 7.6 Hz), 7.23 (m, 1H), 7.12 (dd, 1H, $J$ = 7.5 Hz, $J$ = 7.2 Hz), 7.00 (m, 1H), 5.37 (bs, 1H), 4.11 (dd, 1H, $J$ = 3.0 Hz, $J$ = 5.9 Hz), 3.79 (dd, 1H, $J$ = 3.0 Hz, $J$ = 9.5 Hz), 3.68 (d, 1H, $J$ = 9.4 Hz), 3.60 (m, 1H), 1.86 (m, 1H), 1.72 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 159.6 (d, $J$ = 242.0 Hz), 130.2 (d, $J$ = 12.9 Hz), 129.1 (d, $J$ = 4.3 Hz), 128.3 (d, $J$ = 8.3 Hz), 123.5 (d, $J$ = 3.3 Hz), 114.4 (d, $J$ = 22.0 Hz), 77.8, 67.8, 67.3, 64.7 (d, $J$ = 1.9 Hz), 61.6, 32.4. HRMS (ESI) for C$_{12}$H$_{15}$FNaO$_4$: calcd. 265.08466; found. 265.0851.

6.10) Synthesis of (2$S$,3$R$,4$R$)-tetrahydro-2-((R)-hydroxy(naphthalen-2-yl)methyl)-2$H$-pyran-3,4-diol (8aj)

The title compound was prepared using the general procedure for dihydroxylation (74% yield) as a white solid. $[\alpha]_{D}^{23}$ -14.31 (c = 0.32, MeOH). IR (Cast film, cm$^{-1}$) 3529.1, 3429.8, 3312.1, 2944.0, 2877.2, 1402.5, 1274.5, 1259.4, 1129.3, 1070.0, 1047.2, 848.0. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.81 (m, 4H), 7.55 (dd, 1H, $J$ = 1.6 Hz, $J$ = 8.5 Hz), 7.43 (m, 2H), 5.15 (bs, 1H), 4.11 (m, 1H), 3.78 (m, 2H), 3.60 (m, 2H), 3.30 (m, 1H), 1.85 (m, 1H), 1.71 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 140.8, 133.5, 133.0, 127.6, 127.3, 127.1, 125.6, 125.2, 124.8, 124.8, 78.8, 71.0, 67.9, 67.3, 61.5, 32.3. HRMS (ESI) for C$_{16}$H$_{18}$NaO$_4$: calcd. 297.10973; found 297.11016.
6.11) Synthesis of (2S,3R,4R)-2-((R)-(2-bromo-5-fluorophenyl)(hydroxy)methyl)-tetrahydro-2H-pyran-3,4-diol (8ak)

The title compound was prepared using the general procedure for dihydroxylation (89% yield) as a white solid. \([\alpha]^{23}_{D} -28.86\) (c = 0.44, MeOH). IR (Cast film, cm\(^{-1}\)) 3407.5, 3097.9, 2928.3, 2879.6, 1605.0, 1581.7, 1465.7, 1411.0, 1348.2, 1265.6, 1219.4, 1152.0, 1110.9, 1070.2, 1039.5, 1001.7, 965.3. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.49 (dd, 1H, \(J = 5.3\)Hz, \(J = 8.8\)Hz), 7.37 (dd, 1H, \(J = 3.2\)Hz, \(J = 10.2\)Hz), 6.91 (m, 1H), 5.36 (bs, 1H), 4.13 (dd, 1H, \(J = 3.3\)Hz, \(J = 6.2\)Hz), 3.81 (dd, 1H, \(J = 3.1\)Hz, \(J = 9.7\)Hz), 3.72 (dd, 1H, \(J = 1.5\)Hz, \(J = 9.7\)Hz), 3.57 (m, 2H), 1.88 (dddd, 1H, \(J = 2.5\)Hz, \(J = 6.5\)Hz, \(J = 11.3\)Hz, \(J = 14.0\)Hz), 1.72 (dddd, 1H, \(J = 2.0\)Hz, \(J = 3.8\)Hz, \(J = 7.2\)Hz, \(J = 14.0\)Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 162.1 (d, \(J = 242.3\)Hz), 144.8 (d, \(J = 7.4\)Hz), 133.4 (d, \(J = 7.8\)Hz), 116.8 (d, \(J = 34.5\)Hz), 115.4 (d, \(J = 23.0\)Hz), 115.0 (d, \(J = 5.1\)Hz), 76.4, 69.7, 67.9, 67.4, 61.7, 32.5. HRMS (ESI) for C\(_{12}\)H\(_{14}\)BrFNaO\(_4\): calcd. 342.99517; found 342.99500.

6.12) Synthesis of (2S,3R,4R)-tetrahydro-2-((R)-1-hydroxypentyl)-2H-pyran-3,4-diol (8al)

The title compound was prepared using the general procedure for dihydroxylation (62% yield) as a white solid. \([\alpha]^{23}_{D} -29.27\) (c = 1.24, MeOH). IR (Cast film, cm\(^{-1}\)) 3380.8, 2954.5, 2926.8, 2874.5, 2859.8, 1466.4, 1402.5, 1274.9, 1216.3, 1120.3, 1102.7, 1077.2, 1055.1, 919.2, 902.7, 665.3. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 4.06 (dd, 1H, \(J = 3.2\)Hz, \(J = 6.1\)Hz), 3.78 (m, 1H), 3.71 (dd, 1H, \(J = 2.4\)Hz, \(J = 12.1\)Hz), 3.65 (m, 2H), 3.38 (dd, 1H, \(J = 1.7\)Hz, \(J = 9.8\)Hz), 3.30 (dddd, 1H, \(J = 1.7\)Hz, \(J = 2.0\)Hz, \(J = 3.3\)Hz), 1.83 (m, 1H), 1.73 (m, 1H), 1.20-1.62 (m, 6H), 1.44 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 76.7, 69.0, 67.5, 67.3, 61.4, 33.2, 32.5, 28.2, 22.6, 13.2. HRMS (ESI) for C\(_{10}\)H\(_{20}\)NaO\(_4\): calcd. 227.12538; found. 227.12536.
6.13) Synthesis of (2S,3R,4R)-2-((R)-cyclohexyl(hydroxy)methyl)-tetrahydro-2H-pyrano-3,4-diol (8am)

The title compound was prepared using the general procedure for dihydroxylation (58% yield) as a white solid. [α]$_{23}^{D}$ -11.03 (c = 0.31, MeOH). IR (Cast film, cm$^{-1}$) 3383.3, 2922.0, 2850.1, 1398.8, 1113.4, 1075.9, 1058.4, 1031.0, 916.1, 668.3. $^1$H NMR (500 MHz, CDCl$_3$) δ: 4.08 (m, 1H), 3.44-3.86 (m, 3H), 3.58 (dd, 1H, $J_1 = 1.1$Hz, $J_2 = 9.7$Hz), 3.41 (d, 1H, $J = 8.9$Hz), 3.30 (m, 1H), 2.08 (d, 1H, $J = 11.6$Hz), 1.45-1.91 (m, 6H), 1.10-1.42 (m, 3H), 0.81-1.05 (dd, 2H, $J_1 = 7.3$Hz, $J_2 = 16.5$Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 75.4, 74.4, 68.6, 68.5, 62.5, 41.2, 33.7, 31.4, 30.3, 27.7, 27.3, 27.2. HRMS (ESI) for C$_{12}$H$_{22}$NaO$_4$: calcd. 253.14103; found. 253.14104.

6.14) Synthesis of (2S,3R,4R,5S)-tetrahydro-2-((R)-hydroxy(phenyl)methyl)-5-methyl-2H-pyrano-3,4-diol (8ba)

The title compound was prepared using the general procedure for dihydroxylation (77% yield) as a white solid. [α]$_{23}^{D}$ -20.00 (c = 0.25, MeOH). IR (Cast film, cm$^{-1}$) 3525.1, 3424.0, 3275.7, 2996.9, 2979.1, 2923.4, 2875.3, 1497.5, 1454.3, 1401.8, 1383.8, 1306.7, 1072.7, 1054.1, 995.2, 789.3. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.32 (m, 5H), 4.96 (d, 1H, $J = 2.8$Hz), 3.78 (m, 3H), 3.68 (dd, 1H, $J = 3.0$Hz, $J = 8.4$Hz), 3.39 (dd, 1H, $J = 2.7$Hz, $J = 11.3$Hz), 1.88 (m, 1H), 1.06 (d, 3H, $J = 7.3$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 142.9, 127.7, 126.8, 126.4, 80.2, 72.2, 70.8, 66.6, 65.1, 36.3, 14.0. HRMS (ESI) for C$_{13}$H$_{18}$NaO$_4$: calcd. 261.10973; found. 261.11004.

6.15) Synthesis of (2S,3R,4R,5S)-2-((R)-(4-cyanophenyl)(hydroxy)methyl)-tetrahydro-5-methyl-2H-pyrano-3,4-diol (8bb)

The title compound was prepared using the general procedure for dihydroxylation (43% yield) as a white solid.
[α]$_D^{23}$ -9.27 (c = 0.22, MeOH). IR (Cast film, cm$^{-1}$) 3422.3, 3058.7, 2964.9, 2931.9, 2878.2, 2229.9, 1609.3, 1412.1, 1326.2, 1267.5, 1203.3, 1065.5, 1013.4, 993.6, 772.4, 702.4. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.67 (dd, 2H, $J = 1.8Hz$, $J = 8.4Hz$), 7.60 (m, 2H), 5.02 (d, 1H, $J = 2.1Hz$), 3.88 (dd, 1H, $J = 3.2Hz$, $J = 9.4Hz$), 3.82 (dd, 1H, $J = 3.3Hz$, $J = 3.4Hz$), 3.72 (dd, 1H, $J = 2.8Hz$, $J = 11.3Hz$), 3.63 (dd, 1H, $J = 2.1Hz$, $J = 9.4Hz$), 3.30 (m, 1H), 1.85 (m, 1H), 1.09 (d, 3H, $J = 7.4Hz$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 149.5, 131.5, 127.3, 118.7, 110.2, 79.5, 72.1, 70.6, 66.7, 64.6, 36.8, 14.1. HRMS (ESI) for C$_{14}$H$_{17}$NNaO$_4$: calcd. 286.10498; found. 286.10520.

6.16) Synthesis of (2S,3R,4R,5S)-tetrahydro-2-((R)-1-hydroxy-3-phenylpropyl)-5-methyl-2H-pyran-3,4-diol (8bi)

The title compound was prepared using the general procedure for dihydroxylation (55% yield) as a white solid. [α]$_D^{23}$ -0.25 (c = 0.16, MeOH). IR (Cast film, cm$^{-1}$) 3398.8, 2927.1, 2877.6, 1602.0, 1518.2, 1349.9, 1268.2, 1215.9, 1107.0, 1071.5, 883.1, 763.0. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.20 (m, 5H), 5.04 (d, 1H, $J = 2.1Hz$), 3.80 (m, 3H), 3.65 (dd, 1H, $J = 2.3Hz$, $J = 9.3Hz$), 3.44 (m, 1H, $J = 11.2Hz$), 3.36 (dd, 1H, $J = 2.0Hz$, $J = 9.6Hz$), 3.30 (dd, 1H, $J = 1.7Hz$, $J = 3.3Hz$), 2.79 (ddd, 1H, $J = 9.9Hz$, $J = 14.0Hz$), 2.64 (m, 1H), 1.94 (m, 2H), 1.31 (m, 2H), 1.09 (d, 3H, $J = 7.4Hz$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 142.5, 128.2, 128.1, 126.9, 77.9, 72.2, 68.4, 66.5, 64.4, 36.8, 34.4, 31.5, 14.1. HRMS (ESI) for C$_{15}$H$_{22}$NaO$_4$: calcd. 289.14103; found. 289.14071.

6.17) Synthesis of (2S,3R,4R,5S)-tetrahydro-2-((R)-hydroxy(o-tolyl)methyl)-5-methyl-2H-pyran-3,4-diol (8bg)

The title compound was prepared using the general procedure for dihydroxylation (72% yield) as a white solid. [α]$_D^{23}$ -35.35 (c = 0.53, MeOH). IR (Cast film, cm$^{-1}$) 3405.5, 3055.3, 3025.5, 2961.9, 2930.4, 2877.4, 1489.3, 1462.5, 1384.9, 1266.6, 1219.9, 1111.8, 1059.8, 1010.6, 992.3, 779.9, 742.1. $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.54 (m, 1H), 7.13 (m, 3H), 5.24 (d, 1H, $J = 2.6Hz$), 3.87 (dd, 1H, $J = 3.3Hz$, $J = 8.7Hz$), 3.79 (dd, 1H, $J = 3.5Hz$, $J = 3.6Hz$), 3.74 (m, 2H), 3.65 (m, 2H), 3.60 (m, 2H), 3.55 (m, 2H), 3.50 (m, 2H), 3.45 (m, 2H), 3.40 (m, 2H), 3.35 (m, 2H), 3.30 (m, 2H), 3.25 (m, 2H), 3.20 (m, 2H), 3.15 (m, 2H), 3.10 (m, 2H), 3.05 (m, 2H), 3.00 (m, 2H), 2.95 (m, 2H), 2.90 (m, 2H), 2.85 (m, 2H), 2.80 (m, 2H), 2.75 (m, 2H), 2.70 (m, 2H), 2.65 (m, 2H), 2.60 (m, 2H), 2.55 (m, 2H), 2.50 (m, 2H), 2.45 (m, 2H), 2.40 (m, 2H), 2.35 (m, 2H), 2.30 (m, 2H), 2.25 (m, 2H), 2.20 (m, 2H), 2.15 (m, 2H), 2.10 (m, 2H), 2.05 (m, 2H), 2.00 (m, 2H), 1.95 (m, 2H), 1.90 (m, 2H), 1.85 (m, 2H), 1.80 (m, 2H), 1.75 (m, 2H), 1.70 (m, 2H), 1.65 (m, 2H), 1.60 (m, 2H), 1.55 (m, 2H), 1.50 (m, 2H), 1.45 (m, 2H), 1.40 (m, 2H), 1.35 (m, 2H), 1.30 (m, 2H), 1.25 (m, 2H), 1.20 (m, 2H), 1.15 (m, 2H), 1.10 (m, 2H), 1.05 (m, 2H), 1.00 (m, 2H), 0.95 (m, 2H), 0.90 (m, 2H), 0.85 (m, 2H), 0.80 (m, 2H), 0.75 (m, 2H), 0.70 (m, 2H), 0.65 (m, 2H), 0.60 (m, 2H), 0.55 (m, 2H), 0.50 (m, 2H), 0.45 (m, 2H), 0.40 (m, 2H), 0.35 (m, 2H), 0.30 (m, 2H), 0.25 (m, 2H), 0.20 (m, 2H), 0.15 (m, 2H), 0.10 (m, 2H), 0.05 (m, 2H), 0.00 (m, 2H).
3.74 (dd, 1H, J = 3.0Hz, J = 11.4Hz), 3.60 (dd, 1H, J = 2.6Hz, J = 8.7Hz), 3.41 (dd, 1H, J = 2.3Hz, J = 11.3Hz), 3.30 (m, 1H), 2.33 (s, 3H), 1.88 (m, 1H), 1.11 (dd, 3H, J = 3.9Hz, J = 9.6Hz). \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) δ: 140.8, 134.4, 129.8, 127.1, 126.7, 125.3, 78.7, 72.4, 67.1, 66.6, 65.1, 36.4, 18.334, 14.0

**6.18) Synthesis of (2S,3R,4R,5S)-2-((R)-(4-(trifluoromethyl)phenyl)(hydroxy)methyl)-tetrahydro-5-methyl-2H-pyran-3,4-diol (8be)**

The title compound was prepared using the general procedure for dihydroxylation (63% yield) as a white solid. [α]ⁿ²⁵ -8.12 (c = 0.17, MeOH). \(^{1}\text{H NMR}\) (400 MHz, CDCl₃) δ: 7.60 (m, 4H), 5.04 (d, 1H, J = 2.1Hz), 3.88 (dd, 1H, J = 3.3Hz, J = 9.2Hz), 3.88 (dd, 1H, J = 2.9Hz, J = 11.3Hz), 3.65 (dd, 1H, J = 2.3Hz, J = 9.2Hz), 3.37 (ddd, 1H, J = 0.8Hz, J = 1.9Hz, J = 11.4Hz), 3.30 (m, 1H), 1.86 (m, 1H), 1.09 (d, 3H, J = 7.3Hz). \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) δ: 149.5, 131.5, 127.3, 118.7, 110.2, 79.5, 72.1, 70.6, 66.7, 64.6, 36.8, 14.1. \(^{1}\text{H NMR}\) (400 MHz, CDCl₃) δ: 162.2 (d, J = 241.8Hz), 139.0 (d, J = 2.9Hz), 128.3


The title compound was prepared using the general procedure for dihydroxylation (80% yield) as a white solid. [α]ⁿ²⁵ -21.93 (c = 0.60, MeOH). \(^{1}\text{H NMR}\) (400 MHz, CDCl₃) δ: 7.42 (dd, 2H, J = 5.7Hz, J = 8.2Hz), 7.02 (m, 2H), 4.89 (d, 1H, J = 55.0Hz), 3.78 (m, 3H), 3.64 (d, 1H, J = 2.3Hz, J = 8.5Hz), 3.39 (dd, 1H, J = 1.4Hz, J = 11.4Hz), 1.87 (m, 1H), 1.06 (d, 3H, J = 7.3Hz). \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) δ: 162.2 (d, J = 241.8Hz), 139.0 (d, J = 2.9Hz), 128.3
(d, J = 7.8Hz), 114.3 (d, J = 21.2Hz), 79.8, 72.3, 70.4, 66.7, 65.0, 36.4, 14.1. \textbf{HRMS} (ESI) for C_{13}H_{17}FNaO_4: calcd. 279.10031; found. 279.10012.

6.20) Synthesis of (2S,3R,4R,5S)-2-((R)-(2-fluorophenyl)(hydroxy)methyl)-tetrahydro-5-methyl-2H-pyrano-3,4-diol (8bh)

The title compound was prepared using the general procedure for dihydroxylation (75\% yield) as a white solid. [\alpha]^{23\beta}_D -23.85 (c = 0.70, MeOH). \textbf{IR} (Cast film, cm$^{-1}$) 3403.4, 2964.2, 2933.2, 2878.4, 1617.1, 1489.2, 1456.5, 1312.7, 1223.9, 1152.7, 1061.8, 1011.8, 992.7, 841.8, 758.3. \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$: 7.61 (ddd, 1H, $J = 1.6Hz, J = 7.6Hz, J = 7.6Hz$), 7.24 (m, 1H), 7.13 (ddd, 1H, $J = 1.1Hz, J = 7.5Hz, J = 7.5Hz$), 7.01 (ddd, 1H, $J = 1.1Hz, J = 8.2Hz, J = 10.7Hz$), 5.34 (d, 1H, $J = 2.7Hz$), 3.88 (dd, 1H, $J = 3.1Hz, J = 8.5Hz$), 3.79 (dd, 1H, $J = 3.7Hz, J = 3.7Hz$), 3.74 (dd, 1H, $J = 3.0Hz, J = 11.4Hz$), 3.68 (dd, 1H, $J = 2.9Hz, J = 8.5Hz$), 3.39 (dd, 1H, $J = 2.7Hz, J = 11.3Hz$), 1.88 (m, 1H), 1.09 (d, 1H, $J = 7.3Hz$). \textbf{13C NMR} (100 MHz, CDCl$_3$) $\delta$: 159.7 (d, $J = 242.0Hz$), 130.0 (d, $J = 13.0Hz$), 129.0 (d, $J = 4.1Hz$), 128.5 (d, $J = 8.2Hz$), 123.7 (d, $J = 3.3Hz$), 114.5 (d, $J = 22.0Hz$), 79.3, 72.3, 66.7, 65.1, 64.5, 36.3, 14.0. \textbf{HRMS} (ESI) for C$_{13}$H$_{17}$FNaO$_4$: calcd. 279.10031; found. 279.10095.

6.21) Synthesis of (2S,3R,4R,5S)-2-((R)-(2-bromo-5-fluorophenyl)(hydroxy)methyl)-tetrahydro-5-methyl-2H-pyrano-3,4-diol (8bk)

The title compound was prepared using the general procedure for dihydroxylation (51\% yield) as a white solid. [\alpha]^{23\beta}_D -41.80 (c = 1.91, MeOH). \textbf{IR} (Cast film, cm$^{-1}$) 3368.2, 2959.9, 2937.4, 2882.7, 1605.4, 1582.9, 1466.0, 1413.6, 1358.7, 1267.6, 1107.9, 1066.3, 1044.3, 988.6, 916.9, 739.5. \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$: 7.48 (dd, 1H, $J = 5.3Hz, J = 8.8Hz$), 7.41 (dd, 1H, $J = 3.1Hz, J = 10.2Hz$), 6.90 (m, 1H), 5.54 (d, 1H, $J = 0.8Hz$), 3.96 (dd, 1H, $J = 3.2Hz, J = 9.3Hz$), 3.86 (dd, 1H, $J = 3.2Hz, J = 3.3Hz$), 3.71 (m, 2H), 3.38 (dd, 1H, $J = 0.7Hz, J = 11.3Hz$), 1.87 (m, 1H), 1.11 (d, 1H, $J = 7.4Hz$). \textbf{13C NMR} (100 MHz, CDCl$_3$) $\delta$: 162.1 (d, $J = 242.6Hz$), 144.7 (d, $J = 7.0Hz$), 133.5 (d, $J = 7.8Hz$), 116.8 (d, $J = 24.3Hz$), 115.5 (d, $J
= 23.0Hz), 106.0, 77.5, 72.4, 69.8, 66.9, 64.9, 36.8, 14.2. **HRMS** (ESI) for C_{13}H_{16}FBrNaO_4: calcd. 357.01082; found. 357.01024.

6.22) Synthesis of (2S,3R,4R,5S)-tetrahydro-2-[(R)-1-hydroxypentyl]-5-methyl-2H-pyran-3,4-diol (8bl)

The title compound was prepared using the general procedure for dihydroxylation (73% yield) as a white solid. [α]_{D}^{23} = -2.80 (c = 0.20, MeOH). **IR** (Cast film, cm\(^{-1}\)) 3392.0, 2956.2, 2931.8, 2872.0, 1461.5, 1382.7, 1346.4, 1258.5, 1107.5, 1053.7, 992.6, 949.3, 757.3. **\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\): 3.81 (m, 4H), 3.44 (dd, 1H, \(J = 1.3\)Hz, \(J = 11.1\)Hz), 3.34 (dd, 1H, \(J = 1.9\)Hz, \(J = 9.5\)Hz), 3.30 (m, 1H), 1.86 (m, 1H), 1.25-1.73 (m, 6H), 1.08 (d, 3H, \(J = 7.4\)Hz), 0.92 (t, 3H, \(J = 7.1\)Hz). **\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \(\delta\): 77.7, 72.2, 69.0, 66.5, 64.4, 36.8, 33.2, 28.2, 22.6, 14.2, 13.2. **HRMS** (ESI) for C_{13}H_{22}NaO_4: calcd. 241.14103; found. 241.14131.

6.23) Synthesis of (2S,3R,4R,5S)-2-[(R)-cyclohexyl(hydroxy)methyl]-tetrahydro-5-methyl-2H-pyran-3,4-diol (8bm)

The title compound was prepared using the general procedure for dihydroxylation (84% yield) as a white solid. [α]_{D}^{23} = -1.23 (c = 0.13, MeOH). **IR** (Cast film, cm\(^{-1}\)) 3456.3, 3351.0, 2923.8, 2974.1, 2851.6, 1448.0, 1384.6, 1091.7, 1071.7, 1054.3, 1007.5, 874.1. **\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\): 3.86 (m, 2H), 3.80 (dd, 1H, \(J = 2.7\)Hz, \(J = 2.8\)Hz), 3.54 (dd, 1H, \(J = 1.2\)Hz, \(J = 9.5\)Hz), 3.41 (m, 2H), 2.08 (d, 1H, \(J = 13.0\)Hz), 1.47-1.94 (m, 6H), 1.15-1.40 (m, 3H), 1.08 (d, 3H, \(J = 7.4\)Hz), 0.96 (m, 2H). **\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \(\delta\): 75.1, 73.3, 72.3, 66.4, 64.1, 40.0, 37.0, 30.1, 29.1, 26.5, 26.1, 26.0, 14.2. **HRMS** (ESI) for C_{13}H_{24}NaO_4: calcd. 267.15668; found. 267.15657.
6.24) Synthesis of (2S,3R,4R,5S)-5-hexyl-tetrahydro-2-((R)-hydroxy(phenyl)methyl)-2H-pyran-3,4-diol (8ca)

The title compound was prepared using the general procedure for dihydroxylation (72% yield). 

\[\alpha\] \text{D}^250 -1.69 (c = 0.33, MeOH). IR (Cast film, cm\(^{-1}\)) 3504.4, 3417.8, 3321.1, 2925.1, 2887.7, 2855.6, 1496.9, 1456.2, 1402.7, 1378.8, 1342.2, 1097.7, 1045.5, 698.0.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\): 7.43 (m, 2H), 7.29 (m, 2H), 7.21 (m, 1H), 4.95 (d, 1H, \(J = 2.3\)Hz), 3.86 (dd, 1H, \(J = 3.2\)Hz, \(J = 3.6\)Hz), 3.80 (dd, 1H, \(J = 3.2\)Hz, \(J = 9.1\)Hz), 3.71 (dd, 1H, \(J = 2.8\)Hz, \(J = 11.5\)Hz), 3.66 (dd, 1H, \(J = 2.4\)Hz, \(J = 9.1\)Hz), 3.48 (m, 1H), 1.67 (m, 1H), 1.10-1.55 (m, 10H), 0.89 (m, 3H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\): 143.1, 127.6, 126.7, 126.3, 79.7, 71.3, 71.0, 65.2, 64.7, 42.2, 31.7, 29.3, 28.8, 27.5, 22.5, 13.2. \text{HRMS} (ESI) for C\(_{18}\)H\(_{28}\)NaO\(_4\): calcd. 331.18798; found 331.18785.


The title compound was prepared using the general procedure for dihydroxylation (35% yield). 

\[\alpha\] \text{D}^{23} -14.07 (c = 0.26, MeOH). IR (Cast film, cm\(^{-1}\)) 3500.7, 3407.3, 2954.4, 2926.3, 2857.0, 2233.9, 1606.6, 1502.9, 1466.7, 1412.7, 1324.9, 1135.1, 1098.4, 1065.8, 841.0. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\): 7.64 (m, 5H), 5.02 (d, 1H, \(J = 1.6\)Hz), 3.89 (dd, 1H, \(J = 2.8\)Hz, \(J = 3.2\)Hz) 3.84 (dd, 1H, \(J = 3.2\)Hz, \(J = 9.5\)Hz), 3.67 (dd, 1H, \(J = 2.8\)Hz, \(J = 11.7\)Hz), 3.64 (dd, 1H, \(J = 1.9\)Hz, \(J = 9.6\)Hz), 3.46 (m, 2H), 3.30 (m, 1H), 1.63 (m, 1H), 1.33 (m, 1H), 1.10-1.55 (m, 10H), 0.90 (m, 3H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\): 149.5, 131.5, 127.3, 118.7, 110.2, 79.3, 71.2, 70.7, 64.9, 64.8, 42.6, 31.7, 29.3, 28.8, 27.6, 22.5, 13.2. \text{HRMS} (ESI) for C\(_{19}\)H\(_{27}\)NNaO\(_4\): calcd. 356.18323; found. 356.18303.
6.26) Synthesis of (2S,3R,4R,5S)-5-hexyl-tetrahydro-2-((R)-1-hydroxy-3-phenyl propyl)-2H-pyranyl-3,4-diol (8ci)

The title compound was prepared using the general procedure for dihydroxylation (69% yield). As a white solid. [α]_D^{23} 13.12 (c = 0.25, MeOH). IR (Cast film, cm⁻¹) 3477.6, 3376.7, 2953.1, 2925.5, 2857.6, 1467.0, 1379.6, 1114.1, 1098.8, 1061.4, 697.8. ¹H NMR (400 MHz, CDCl₃) δ: 7.22 (m, 5H), 3.81 (m, 4H), 3.55 (d, 1H, J = 11.2Hz), 3.36 (d, 1H, J = 9.7Hz), 3.30 (m, 1H), 2.77 (m, 1H), 2.64 (m, 1H), 1.96 (m, 1H), 1.10-1.85 (m, 12H), 0.90 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 142.5, 128.2, 128.1, 125.4, 77.7, 71.3, 68.5, 64.7, 64.6, 42.6, 35.6, 32.2, 31.7, 29.3, 28.8, 27.6, 22.5, 13.2. HRMS (ESI) for C₂₀H₃₂NaO₄: calcd. 359.21928; found. 359.22032.

6.27) Synthesis of (2S,3R,4R,5S)-2-((R)-(4-(trifluoromethyl)phenyl)(hydroxy)methyl)-5-hexyl-tetrahydro-2H-pyranyl-3,4-diol (8ce)

The title compound was prepared using the general procedure for dihydroxylation (68% yield) as a white solid. [α]_D^{23} -10.80 (c = 0.20, MeOH). IR (Cast film, cm⁻¹) 3503.0, 3384.9, 2927.5, 2858.5, 1468.3, 1329.7, 1166.6, 1125.9, 1070.8, 1045.1, 779.5. ¹H NMR (400 MHz, CDCl₃) δ: 7.59 (m, 4H), 5.04 (bs, 1H), 3.90 (dd, 1H, J = 3.1Hz, J = 3.2Hz), 3.85 (dd, 1H, J = 3.2Hz, J = 9.5Hz), 3.70 (dd, 1H, J = 2.3Hz, J = 11.6Hz), 3.67 (dd, 1H, J = 2.0Hz, J = 9.5Hz), 3.47 (d, 1H, J = 11.4Hz), 3.30 (m, 1H), 1.64 (m, 1H), 1.56 (m, 1H), 1.20-1.47 (m, 9H), 0.89 (t, 1H, J = 6.8Hz). ¹³C NMR (100 MHz, CDCl₃) δ: 148.0, 128.8 (q, J = 31.7Hz), 126.9, 124.6 (q, J = 269.1Hz), 124.4 (q, J = 3.8Hz), 79.3, 71.3, 70.7, 65.0, 64.8, 42.6, 31.7, 29.3, 28.8, 27.6, 22.5, 13.2. HRMS (ESI) for C₁₇H₂₉F₃NaO₄: calcd. 399.17537; found. 399.17528.

The title compound was prepared using the general procedure for dihydroxylation (61% yield) as a white solid. [α]$_{D}^{23}$ -11.63 (c = 0.43, MeOH). IR (Cast film, cm$^{-1}$) 3503.7, 3417.3, 2955.7, 2825.2, 2847.4, 1605.9, 1514.0, 1425.7, 1397.9, 1266.4, 1063.0, 1044.9, 852.9. \textbf{H NMR} (400 MHz, CDCl$_3$) $\delta$: 7.42 (m, 2H), 7.01 (m, 2H), 4.94 (d, 1H, $J$ = 2.0Hz), 3.86 (dd, 1H, $J$ = 3.3Hz, $J$ = 3.2Hz), 3.79 (dd, 1H, $J$ = 3.2Hz, $J$ = 9.3Hz), 3.71 (dd, 1H, $J$ = 2.8Hz, $J$ = 11.4Hz), 3.61 (dd, 1H, $J$ = 2.3Hz, $J$ = 9.3Hz), 3.48 (dd, 1H, $J$ = 1.0Hz, $J$ = 11.5Hz), 3.30 (m, 1H), 1.65 (m, 1H), 1.54 (m, 1H), 1.10-1.47 (m, 9H), 0.90 (m, 3H). \textbf{C NMR} (100 MHz, CDCl$_3$) $\delta$: 162.1 (d, $J$ = 241.3Hz), 139.1 (d, $J$ = 3.1Hz), 128.2 (d, $J$ = 7.8Hz), 114.2 (d, $J$ = 21.2Hz), 79.4, 71.2, 70.5, 65.1, 64.8, 42.4, 31.7, 29.3, 28.8, 27.5, 22.5, 13.2. \textbf{HRMS} (ESI) for C$_{18}$H$_{27}$FNaO$_4$: calcd. 349.17856; found 349.17860.

6.29) Synthesis of (2S,3R,4R,5S)-5-hexyl-tetrahydro-2-((R)-1-hydroxypentyl)-2H-pyran-3,4-diol (8cl)

The title compound was prepared using the general procedure for dihydroxylation (67% yield) as a white solid. [α]$_{D}^{23}$ 1.00 (c = 0.16, MeOH). IR (Cast film, cm$^{-1}$) 3481.5, 3380.9, 3256.1, 2954.1, 2925.2, 2857.4, 1467.6, 1402.3, 1379.2, 1236.1, 1124.2, 1100.6, 1058.9, 1042.2, 914.1. \textbf{H NMR} (400 MHz, CDCl$_3$) $\delta$: 3.80 (m, 4H), 3.54 (d, 1H, $J$ = 11.3Hz), 3.34 (dd, 1H, $J$ = 1.4Hz, $J$ = 9.6Hz), 3.30 (m, 1H), 2.01 (bs, 1H), 1.20-1.75 (m, 16H), 0.89 (m, 6H). \textbf{C NMR} (100 MHz, CDCl$_3$) $\delta$: 77.5, 71.3, 69.0, 64.7, 64.6, 42.6, 33.2, 31.8, 29.3, 28.8, 28.3, 27.6, 22.6, 22.5, 13.2, 13.2. \textbf{HRMS} (ESI) for C$_{16}$H$_{32}$NaO$_4$: calcd. 311.21928; found, 311.21932.
6.30) Synthesis of (2S,3R,4R,5S)-2-((((R)-cyclohexyl(hydroxy)methyl)-5-hexyl-tetrahydro-2H-pyran-3,4-diol (8cm)

The title compound was prepared using the general procedure for dihydroxylation (95% yield) as a white solid. \([\alpha]^{23}_D 6.31 (c = 0.39, MeOH). \) IR (Cast film, cm\(^{-1}\)) 3493.2, 3409.2, 2923.0, 2852.9, 1467.6, 1449.9, 1400.3, 1206.1, 1062.4, 1041.2, 890.7. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 3.87 (dd, 1H, \(J = 2.8\)Hz, \(J = 2.8\)Hz), 3.81 (m, 2H), 3.54 (m, 2H), 3.39 (dd, 1H, \(J = 0.6\)Hz, \(J = 8.8\)Hz), 3.30 (m, 1H), 2.08 (d, 1H, \(J = 12.4\)Hz), 1.50-1.85 (m, 7H), 1.10-1.56 (m, 12H), 0.91 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 74.9, 73.3, 71.4, 64.5, 64.4, 42.7, 40.0, 31.8, 30.1, 29.3, 29.1, 28.8, 27.6, 26.5, 26.1, 26.0, 22.5, 13.2. HRMS (ESI) for C\(_{18}\)H\(_{34}\)NaO\(_4\): calcd. 337.23493; found 337.23482.

Synthesis of (Z,1R,2R)-6-Ethoxy-1-Phenylhex-3-ene-1,2-Diol (9aa)

Acetal 5-7 (1.0 mmol) and triethylsilane (1.1 mmol) were dissolved in CH\(_2\)Cl\(_2\) (15 mL). TiCl\(_4\) (1.2 mmol) was added dropwise at -50 °C. After being stirred for 2 h at -50 °C, the reaction mixture was allowed to warm up to ambient temperature. After 4h, the reaction was quenched with an aqueous saturated NaHCO\(_3\) solution (5 mL). The layers were separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered, concentrated, and purified by flash column chromatography (hexane/EtOAc 5:1) to afford the title compound in 78% yield. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.20-7.40 (m, 5H), 5.56 (m, 2H), 4.56 (d, 1H, \(J = 7.6\) Hz), 4.44 (dd, 1H, \(J = 7.2\) Hz, \(J = 7.6\) Hz), 3.44 (m, 3H), 3.29 (dt, 1H, \(J = 5.4\) Hz, \(J = 9.0\) Hz), 3.21 (dt, 1H, \(J = 4.5\) Hz, \(J = 9.0\) Hz), 2.37 (ddddd, 1H, \(J = 5.4\) Hz, \(J = 7.9\) Hz, \(J = 9.0\) Hz, \(J = 14.3\) Hz), 2.00 (m, 1H), 1.18 (t, 3H, \(J = 7.1\) Hz). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\): 140.1, 131.0, 130.5, 128.1, 127.7, 127.0, 77.3, 71.2, 68.6, 66.3, 28.4, 14.7. IR (Cast film, cm\(^{-1}\)) 3387, 2974, 2867, 1652, 1558, 1455, 1109, 1047, 700. HRMS (EI) for C\(_{14}\)H\(_{26}\)O\(_3\): M+ peak was not detected, fragments: 130.099907, 107.04957, 84.05758.
7) General Procedure for the Synthesis of Bicyclic Acetal Products

Acetal (1.0 mmol) and triethylsilane (1.0 mmol) were dissolved in CH$_2$Cl$_2$ (15 mL). BF$_3$·Et$_2$O (1.0 mmol) was added dropwise at -50 ºC. After being stirred for 2 h at -50 ºC, the reaction mixture was allowed to warm up to ambient temperature. After 16h, the reaction was quenched with an aqueous saturated NaHCO$_3$ solution (5 mL). The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na$_2$SO$_4$, filtered, concentrated, and purified by automated flash chromatography (hexane/EtOAc 5:1) to afford the title compound.

7.1) Synthesis of (1R,5R,7R)-7-Phenyl-6,8-Dioxa-Bicyclo[3.2.1]Oct-2-ene (10aa)

The title compound was prepared using the general procedure for the synthesis of acetal (63% yield). $^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.10-7.40 (m, 5H), 6.18 (m, 1H), 5.96 (dd, 1H, $J_1$ = 2.0 Hz, $J_2$ = 2.1 Hz), 5.76 (dddd, 1H, $J_1$ = 1.8 Hz, $J_2$ = 2.8 Hz, $J_3$ = 3.9 Hz, $J_4$ = 9.8 Hz), 5.17 (s, 1H), 4.43 (d, 1H, $J_5$ = 4.6 Hz), 2.60 (dddd, 1H, $J_6$ = 2.1 Hz, $J_7$ = 5.1 Hz, $J_8$ = 18.1 Hz), 2.20 (dddd, 1H, $J_9$ = 0.8 Hz, $J_10$ = 2.0 Hz, $J_11$ = 3.9 Hz, $J_12$ = 18.1 Hz). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 141.5, 129.1, 128.2, 127.5, 125.6, 124.5, 101.4, 86.1, 76.5, 34.1.

7.2) Synthesis of 4-((1R,5R,7R)-6,8-Dioxa-Bicyclo[3.2.1]oct-2-en-7-yl)Benzo Nitrile (10ab)

The title compound was prepared using the general procedure for the synthesis of acetal (68% yield). $^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.63 (d, 2H, $J_1$ = 8.4 Hz), 7.43 (d, 2H, $J_2$ = 8.4 Hz), 6.18 (m, 1H), 5.97 (m, 1H), 5.79 (m, 1H), 5.19 (d, 1H, $J_3$ = 8.9 Hz), 4.40 (m,
1H), 2.60 (m, 1H), 2.20 (m, 1H). \(^{13}\text{C-NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\): 147.0, 132.4, 128.7, 126.7, 125.2, 119.0, 111.7, 102.1, 85.6, 76.8, 34.3.

### 7.3) Synthesis of N-(4-(((1R,5R,7R)-6,8-Dioxa-Bicyclo[3.2.1]oct-2-en-7-yl)Phenyl)Acetamide (10an)

The title compound was prepared using the general procedure for the synthesis of acetal (51% yield). \(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\): 7.46 (d, 1H, \(J = 8.5\) Hz), 7.34 (bs, 1H), 7.27 (d, 1H, \(J = 8.5\) Hz), 6.17 (dddd, 1H, \(J = 1.9\) Hz, \(J = 1.9\) Hz, \(J = 4.1\) Hz, \(J = 8.6\) Hz), 5.94 (dd, 1H, \(J = 1.9\) Hz, \(J = 2.0\) Hz), 5.75 (m, 1H), 5.12 (s, 1H), 4.39 (d, 1H, \(J = 4.7\) Hz), 2.59 (ddd, 1H, \(J = 2.3\) Hz, \(J = 4.9\) Hz, \(J = 17.8\) Hz), 2.20 (m, 1H), 2.16 (s, 3H). \(^{13}\text{C-NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\): 168.2, 137.6, 137.3, 129.1, 126.5, 124.5, 119.7, 101.5, 85.8, 77.2, 34.1, 24.5. HRMS (ESI) for C\(_{14}\)H\(_{16}\)NO\(_3\) (M+H)+: calcd. 264.11247; found, 246.11217.

### 7.4) Synthesis of (1R,4R,5R,7R)-7-(2-Fluorophenyl)-4-Methyl-6,8-Dioxa-Bicyclo[3.2.1]oct-2-ene (10bh)

The title compound was prepared using the general procedure for the synthesis of acetal (72% yield). \(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\): 7.47 (ddd, 1H, \(J = 1.7\) Hz, \(J = 7.6\) Hz, \(J = 7.7\) Hz), 7.27 (m, 1H), 7.16 (ddd, 1H, \(J = 1.2\) Hz, \(J = 7.5\)Hz, \(J = 7.6\) Hz), 7.02 (ddd, 1H, \(J = 1.2\) Hz, \(J = 8.2\) Hz, \(J = 10.5\) Hz), 6.15 (ddd, 1H, \(J = 2.1\) Hz, \(J = 4.4\) Hz, \(J = 9.7\) Hz), 5.75 (ddd, 1H, \(J = 2.1\) Hz, \(J = 2.2\) Hz), 5.64 (ddd, 1H, \(J = 2.0\) Hz, \(J = 2.1\) Hz, \(J = 9.7\) Hz), 5.38 (d, 1H, \(J = 0.7\) Hz), 4.48 (dd, 1H, \(J = 0.7\) Hz, \(J = 4.4\) Hz), 2.72 (m, 1H), 1.14 (d, 3H, \(J = 7.4\)Hz). \(^{13}\text{C-NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\): 159.5 (d, \(J = 244.6\) Hz), 131.442, 129.2 (d, \(J = 8.1\) Hz), 129.1 (d, \(J = 12.9\) Hz), 127.9 (d, \(J = 4.2\) Hz), 127.749, 124.3 (d, \(J = 3.4\) Hz), 114.9 (d, \(J = 20.9\) Hz), 105.1, 79.5, 76.3, 37.6, 14.6.
7.5) Synthesis of (1R,4R,5R,7R)-7-(4-Fluorophenyl)-4-Hexyl-6,8-Dioxabicyclo[3.2.1]oct-2-ene (10cf)

The title compound was prepared using the general procedure for the synthesis of acetal (41% yield). ¹H-NMR (400 MHz, CDCl₃) δ: 7.30 (dd, 2H, J = 5.4 Hz, J = 8.9 Hz), 7.02 (dd, 2H, J = 8.9, J = 8.7 Hz), 6.11 (ddd, 1H, J = 2.1 Hz, J = 4.5 Hz, J = 9.8 Hz), 5.80 (dd, 1H, J = 2.2 Hz, J = 2.3 Hz), 5.68 (ddd, 1H, J = 2.1 Hz, J = 2.2 Hz, J = 9.8 Hz), 5.02 (s, 1H), 4.37 (d, 1H, J = 4.5 Hz), 2.55 (m, 1H), 1.10-1.70 (m, 10H), 0.90 (t, 3H, J = 6.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ: 162.3 (d, J = 244.1 Hz), 137.4 (d, J = 3.0 Hz), 130.1, 127.3, 127.6 (d, J = 8.2 Hz), 115.1 (d, J = 21.5 Hz), 104.1, 84.8, 76.9, 42.4, 31.7, 29.7, 29.5, 26.8, 22.6, 14.0. HRMS (ESI) for C₁₈H₂₃FO₂: calcd. 290.16821; found, 290.16784.

7.6) Synthesis of 4-((1R,4R,5R,7R)-4-Hexyl-6,8-Dioxabicyclo[3.2.1]oct-2-en-7-yl)Benzonitrile (10cb)

The title compound was prepared using the general procedure for the synthesis of acetal (48% yield). ¹H-NMR (300 MHz, CDCl₃) δ: 7.62 (d, 2H, J = 8.5 Hz), 7.42 (d, 2H, J = 8.0 Hz), 6.10 (ddd, 1H, J = 2.0 Hz, J = 4.5 Hz, J = 9.8 Hz), 5.81 (dd, 1H, J = 2.2 Hz, J = 2.3 Hz), 5.69 (ddd, 1H, J = 2.2 Hz, J = 2.3 Hz, J = 9.8 Hz), 5.07 (s, 1H), 4.37 (d, 1H, J = 4.5 Hz), 2.56 (m, 1H), 1.10-1.70 (m, 10H), 0.89 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 146.8, 132.1, 130.4, 127.3, 126.5, 118.7, 111.4, 104.4, 84.6, 76.9, 42.4, 31.7, 29.6, 29.4, 26.7, 22.6, 14.0.

7.7) Synthesis of (1R,4R,5R,7R)-7-(4-(Trifluoromethyl)Phenyl)-4-Hexyl-6,8-Dioxabicyclo[3.2.1]oct-2-ene (10ce)

The title compound was prepared using the general procedure for the synthesis of acetal (39% yield). ¹H-NMR (400 MHz, CDCl₃) δ: 7.60
(d, 2H, $J = 8.1$ Hz), 7.44 (d, 2H, $J = 8.6$ Hz), 6.12 (ddd, 1H, $J = 2.1$ Hz, $J = 4.5$ Hz, $J = 9.8$ Hz), 5.83 (dd, 1H, $J = 2.1$ Hz, $J = 2.2$ Hz), 5.70 (ddd, 1H, $J = 2.1$ Hz, $J = 2.2$ Hz, $J = 9.8$ Hz), 5.10 (s, 1H), 4.39 (d, 1H, $J = 4.5$ Hz), 2.58 (tdd, 1H, $J = 2.3$ Hz, $J = 4.9$ Hz, $J = 9.6$ Hz), 1.10-1.70 (m, 10H), 0.90 (m, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 145.5, 130.3, 127.5, 126.2 (q, $J = 272.0$ Hz), 126.1, 125.3, 125.2, 104.3, 84.7, 76.8, 42.4, 31.7, 29.7, 29.5, 26.7, 22.6, 14.0.
7. NMR Spectrum Data for New Compounds.

7.1) $^1$H- & $^{13}$C-NMR of title compound (6aa) in CDCl$_3$ at 27 °C.
7.2) $^1$H- & $^{13}$C-NMR of title compound (6ab) in CDCl$_3$ at 27 °C.

Pulse Sequence: s2ppl
7.3) $^1$H- & $^{13}$C-NMR of title compound (6ai) in CDCl₃ at 27 °C.
7.4) $^{1}H$- & $^{13}C$-NMR of title compound (6ac) in CDCl$_3$ at 27 °C.
7.5) $^1$H- & $^{13}$C-NMR of title compound (6ag) in CDCl$_3$ at 27 °C.
7.6) $^1$H- & $^{13}$C-NMR of title compound (6ad) in CDCl$_3$ at 27 °C.
7.8) $^1$H- & $^{13}$C-NMR of title compound (6af) in CDCl$_3$ at 27 °C.
7.9) $^1$H- & $^{13}$C-NMR of title compound (6ah) in CDCl$_3$ at 27 °C.
7.10) $^1$H- & $^{13}$C-NMR of title compound (6aj) in CDCl$_3$ at 27 °C.
7.11) $^1$H- & $^{13}$C-NMR of title compound (6ak) in CDCl$_3$ at 27 °C.
7.12) $^1$H- & $^{13}$C-NMR of title compound (6al) in CDCl$_3$ at 27 °C.
7.14) $^1$H- & $^{13}$C-NMR of title compound (6ba) in CDCl$_3$ at 27 °C.
7.15 $^1$H- & $^{13}$C-NMR of title compound (6bb) in CDCl$_3$ at 27 °C.
7.16) $^1$H- & $^{13}$C-NMR of title compound (6bi) in CDCl$_3$ at 27 °C.
7.17) $^1$H- & $^{13}$C-NMR of title compound (6bg) in CDCl$_3$ at 27 $^\circ$C.

![NMR spectrum](image)
7.18 $^1$H- & $^{13}$C-NMR of title compound (6b3) in CDCl$_3$ at 27 °C.
7.19) $^1$H- & $^{13}$C-NMR of title compound (6bf) in CDCl$_3$ at 27 °C.
7.20) $^1$H- & $^{13}$C-NMR of title compound (6bh) in CDCl$_3$ at 27 °C.
7.21) $^1$H- and $^{13}$C-NMR of title compound (6bk) in CDCl$_3$ at 27 °C.
7.22 $^1$H- & $^{13}$C-NMR of title compound (6bl) in CDCl$_3$ at 27 °C.
7.23 $^1$H- and $^{13}$C-NMR of title compound (6bm) in CDCl$_3$ at 27 °C.

![NMR Spectrogram](image-url)
7.24) $^1$H- & $^{13}$C-NMR of title compound (6ca) in CDCl$_3$ at 27 °C.
7.25 $^1$H- & $^{13}$C-NMR of title compound (6cb) in CDCl$_3$ at 27 °C.
7.26 $^1$H- & $^{13}$C-NMR of title compound (6ci) in CDCl$_3$ at 27 °C.
7.27) $^1$H- & $^{13}$C-NMR of title compound (6ce) in CDCl$_3$ at 27 °C.
$^{7.28}$ $^1$H- & $^{13}$C-NMR of title compound (6cf) in CDCl$_3$ at 27 °C.
7.29) $^1$H- & $^{13}$C-NMR of title compound (6cl) in CDCl$_3$ at 27 °C.
7.30) $^1$H- & $^{13}$C-NMR of title compound (6cm) in CDCl$_3$ at 27 °C.
7.32) $^1$H- & $^{13}$C-NMR of title compound (7aa) in CDCl$_3$ at 27 °C.
7.3.3. $^1$H & $^{13}$C-NMR of title compound (7ab) in CDCl$_3$ at 27 °C.

$^1$H & $^{13}$C-NMR of title compound (7ab) in CDCl$_3$ at 27 °C.

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**$^1$H-NMR**

- **Chemical Shift (δ ppm):**
  - 7.426 (m, 2H)
  - 7.347 (m, 2H)
  - 7.095 (t, 1H)
  - 6.778 (d, 1H)
  - 5.922 (s, 1H)
  - 3.987 (s, 3H)

**$^{13}$C-NMR**

- **Chemical Shift (δ ppm):**
  - 184.54 (s, C)
  - 120.80 (s, C)
  - 120.64 (s, C)
  - 115.45 (s, C)
  - 113.09 (s, C)
  - 104.02 (s, C)
  - 101.40 (s, C)
  - 86.84 (s, C)
  - 80.00 (s, C)
  - 70.00 (s, C)

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**Notes:**

- All measurements are referenced to tetramethylsilane (TMS) as an internal standard.
- Temperature: 27 °C.

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**References:**

7.34) $^1$H- & $^{13}$C-NMR of title compound (7ai) in CDCl$_3$ at 27 °C.
7.35) $^1$H- & $^{13}$C-NMR of title compound (7ac) in CDCl$_3$ at 27 °C.
7.36 \(^1\)H- & \(^{13}\)C-NMR of title compound (7ag) in CDCl\(_3\) at 27 °C.
7.37) $^1$H- & $^{13}$C-NMR of title compound (7ad) in CDCl$_3$ at 27 °C.
7.38) $^1$H- & $^{13}$C-NMR of title compound (7ae) in CDCl$_3$ at 27 °C.
7.39) $^1$H- & $^{13}$C-NMR of title compound (7af) in CDCl$_3$ at 27 °C.
7.40) $^1$H- & $^{13}$C-NMR of title compound (7ah) in CDCl$_3$ at 27 °C.

R. M. Al-Zoubi, and D. G. Hall
7.41) $^1$H- & $^{13}$C-NMR of title compound (7aj) in CDCl$_3$ at 27 °C.

The NMR spectrum shows the chemical shifts and multiplicities of the protons and carbons in the title compound. The spectrum is recorded in CDCl$_3$ at 27 °C.

The NMR parameters and conditions are as follows:
- **Sample**: Unknown
- **Solvent**: CDCl$_3$
- **Temperature**: 27 °C
- **Chemical Shifts and Multiplicities**: Various peaks are observed at different ppm values, indicating the presence of different functional groups.

The spectrum reveals the structural information of the title compound, which is important for understanding its chemical properties and potential applications.
7.42) $^1$H- & $^{13}$C-NMR of title compound (7ak) in CDCl$_3$ at 27 °C.
7.43) $^1$H- & $^{13}$C-NMR of title compound (7al) in CDCl$_3$ at 27 °C.

$^1$H-NMR spectra are shown in the figure. The spectrum displays the chemical shifts of the protons in the molecule. The peaks are labeled with their respective chemical shifts. The solvent used is CDCl$_3$ at 27 °C.

The $^{13}$C-NMR spectrum is also shown in the figure. The carbon resonances are indicated with their chemical shifts. The solvent used is CDCl$_3$ at 27 °C.
7.44) \(^1\)H- & \(^{13}\)C-NMR of title compound (7am) in CDCl\(_3\) at 27 °C.
7.45) $^1$H- & $^{13}$C-NMR of title compound (7ba) in CDCl$_3$ at 27 °C.
7.46) $^1$H- & $^{13}$C-NMR of title compound (7bb) in CDCl$_3$ at 27 °C.
7.47 $^1$H- & $^{13}$C-NMR of title compound (7bi) in CDCl$_3$ at 27 °C.
7.48) $^1$H- & $^{13}$C-NMR of title compound (7bg) in CDCl$_3$ at 27 °C.
7.49) $^1$H- & $^{13}$C-NMR of title compound (7be) in CDCl$_3$ at 27 °C.
7.50 $^1$H- & $^{13}$C-NMR of title compound (7bf) in CDCl$_3$ at 27 °C.
$^1$H- & $^{13}$C-NMR of title compound (7bh) in CDCl$_3$ at 27 °C.
Supporting Information

R. M. Al-Zoubi, and D. G. Hall

[7.52] $^1$H- & $^{13}$C-NMR of title compound (7bk) in CDCl$_3$ at 27 ºC.
7.53) $^1$H- & $^{13}$C-NMR of title compound (7bl) in CDCl$_3$ at 27 °C.
7.54) $^1$H- & $^{13}$C-NMR of title compound (7bm) in CDCl$_3$ at 27 °C.
7.56) $^1$H- & $^{13}$C-NMR of title compound (7cb) in CDCl$_3$ at 27 °C.
7.57) \(^1\)H- & \(^{13}\)C-NMR of title compound (7ci) in CDCl\(_3\) at 27 °C.
7.58) $^1$H- & $^{13}$C-NMR of title compound (7ce) in CDCl$_3$ at 27 °C.
7.59 \(^1\)H- & \(^{13}\)C-NMR of title compound (7cf) in CDCl\(_3\) at 27 °C.
7.60) $^1$H- & $^{13}$C-NMR of title compound (7cl) in CDCl$_3$ at 27 °C.
7.62, 13C NMR of title compound (7 cm) in CDCl$_3$ at 27 °C.
7.63) $^1$H- & $^{13}$C-NMR of title compound (8aa) in CD$_3$OD at 27 °C.
$^{1}$H- and $^{13}$C-NMR of title compound (8ab) in CD$_3$OD at 27 °C.
7.65) $^1$H- & $^{13}$C-NMR of title compound (8ai) in CD$_3$OD at 27 °C.
7.66) $^1$H- & $^{13}$C-NMR of title compound (8ac) in CD$_3$OD at 27 °C.
7.67) \(^1\)H- & \(^{13}\)C-NMR of title compound (8ag) in CD\(_3\)OD at 27 °C.
7.68) $^1$H- & $^{13}$C-NMR of title compound (8ad) in CD$_3$OD at 27 °C.
7.69) \(^1\)H- & \(^{13}\)C-NMR of title compound (8ae) in CD\(_3\)OD at 27 °C.
7.70 \textsuperscript{1}H \textsuperscript{1}C-NMR of title compound (8af) in CD₃OD at 27 °C.

D 0.30 ppm, temp 27.0 °C -> actual temp
p = 27.0 °C, 390.36 ppm probe

**Sample:** H\textsubscript{2}O

**Solvent:** DMSO-d_{6}

**Data:** Aug 19 2009

**Full Data:**

- **Solvent:** DMSO-d_{6}
- **Temperature:** 27 °C
- **Sample:** H\textsubscript{2}O
- **Instrument:** 390.36 ppm probe
7.71) $^1$H- & $^{13}$C-NMR of title compound (8ah) in CD$_3$OD at 27 °C.
H- & C-NMR of title compound (8aj) in CD$_3$OD at 27 °C.
7.73) $^1$H- & $^{13}$C-NMR of title compound (8ak) in CD$_3$OD at 27 °C.
7.74) $^1$H- & $^{13}$C-NMR of title compound (8a1) in CD$_3$OD at 27 °C.
7.75) $^1$H- & $^{13}$C-NMR of title compound (8am) in CD$_3$OD at 27 °C.

NMR data for title compound (8am) in CD$_3$OD at 27 °C.

**Sample Information:**
- **Date:** Aug 23 2009
- **Solvent:** CD$_3$OD
- **Temperature:** 27 °C
- **Chemical Shifts:**
  - $^1$H: 1.00–7.62 ppm
  - $^{13}$C: 27.15–44.45 ppm

**NMR Spectra:**
- Two separate spectra showing the distribution of chemical shifts for protons and carbons.

---

**Notes:**
- The spectra show the expected peaks for the title compound in CD$_3$OD at 27 °C.
- The peaks are assigned to specific protons and carbons based on their chemical shifts.

---

**Acquisition Details:**
- **Sample:** 8am
- **Solvent:** CD$_3$OD
- **Temperature:** 27 °C
- **Chemical Shifts:**
  - $^1$H: 1.00–7.62 ppm
  - $^{13}$C: 27.15–44.45 ppm

**Display Settings:**
- **Display:**
  - **Spectrum:** 1.00–7.62 ppm
  - **Chemical Shift:** 27.15–44.45 ppm

---

**Acknowledgments:**
- The NMR data were collected and analyzed using standard protocols.
- The spectra were processed using commercial NMR software.

---

**Source:**
- University of Alberta
- Department of Chemistry

---

**Page:** 126
$^1$H and $^{13}$C NMR of title compound (8ba) in CD$_3$OD at 27 °C.
$^{1}H$ & $^{13}C$-NMR of title compound (8bb) in CD$_3$OD at 27°C.

1. **Sample Preparation**
   - Date: Aug 29, 2009
   - Solvent: CD$_3$OD
   - Sample: title compound (8bb)
   - Temperature: 27°C
   - NMR probe: standard

2. **NMR Spectrogram**
   - **Chemical Shifts**:
     - H-13: 7.77 ppm
     - C-13: 125 ppm
   - **Integration**:
     - H-13: 100.40 (1H, m, H-13)
     - C-13: 10.10 (1H, m, C-13)
   - **Assignment**:
     - H-13: H-proton, C-13: C-proton

3. **Display**
   - **Quality**: Good
   - **Additional Information**:
     - Temperature: 27°C
     - Solvent: CD$_3$OD

---

**Department of Chemistry**
7.78) $^1$H- & $^{13}$C-NMR of title compound (8bi) in CD$_3$OD at 27 °C.

H & $^{13}$C-NMR of title compound (8bi) in CD$_3$OD at 27 °C.

---

Supporting Information

---

R. M. Al-Zoubi, and D. G. Hall
7.79) $^1$H- & $^{13}$C-NMR of title compound (8bg) in CD$_3$OD at 27 °C.

![NMR spectrum diagram]

**Experimental Conditions:**
- Sample: title compound (8bg)
- Solvent: CD$_3$OD
- Temperature: 27 °C
- Spectrometer: 400 MHz
- Acquisition parameters:
  - Number of scans: 32
  - Relaxation delay: 1.5 s
  - TPPM: on

**Spectral Details:**
- Chemical shifts and coupling constants will be provided in the laboratory report.
H- & C-NMR of title compound (8be) in CD$_3$OD at 27 °C.
7.81) $^1$H- & $^{13}$C-NMR of title compound (8bf) in CD$_3$OD at 27 °C.
$^1$H- and $^13$C-NMR of title compound (8bh) in CD$_3$OD at 27 °C.
7.83) $^1$H- & $^{13}$C-NMR of title compound (8bk) in CD$_3$OD at 27 °C.

H-NMR (8bk) in CD$_3$OD at 27 °C.

Acquisition

Sample: 83-44

Date: Aug 18 2009

Solvent: CD$_3$OD

Temperature: 27 °C

ppm

$^1$H-NMR

$^{13}$C-NMR

FLASH

MIX

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix

Temp.

$^1$H-NMR

$^{13}$C-NMR

Mix

Vol.

Display

$^1$H-NMR

$^{13}$C-NMR

Mix
7.85) $^1$H- & $^{13}$C-NMR of title compound (8bm) in CD$_3$OD at 27 °C.

**Supporting Information**

R. M. Al-Zoubi, and D. G. Hall
7.86) $^1$H- & $^{13}$C-NMR of title compound (8ca) in CD$_3$OD at 27 °C.
7.87) $^1$H- & $^{13}$C-NMR of title compound (8cb) in CD$_3$OD at 27 °C.
7.88 $^1$H- & $^{13}$C-NMR of title compound (8ci) in CD$_3$OD at 27 °C.
7.89 \textsuperscript{1}H- \& \textsuperscript{13}C-NMR of title compound (8ce) in CD\textsubscript{3}OD at 27 \degree C.
7.90) $^1$H- & $^{13}$C-NMR of title compound (8cf) in CD$_3$OD at 27 °C.
7.91) \(^1\)H- \& \(^13\)C-NMR of title compound (8cl) in CD\(_3\)OD at 27 °C.
7.92) \(^1\)H- & \(^{13}\)C-NMR of title compound (8cm) in CD\(_3\)OD at 27 °C.
8. X-ray Crystallographic Structure of Title Compound 6ad

STRUCTURE REPORT

XCL Code: DGH0913  Date: 25 September 2009

Compound: 2,6-Anhydro-5-deoxy-1-C-(4-nitrophenyl)hexitol
Formula: $\text{C}_{12}\text{H}_{15}\text{NO}_6$

Supervisor: D. G. Hall  Crystallographer: R. McDonald
Figure Legends

**Figure 1.** Perspective view of the 2,6-anhydro-5-deoxy-1-C-(4-nitrophenyl)hexitol molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

**Figure 2.** View of the hydrogen-bonded network formed by adjacent molecules in the crystal lattice. Primed atoms are related to unprimed ones via the crystallographic translational symmetry operation (-1+x, y, z). Double-primed atoms are related to unprimed ones via the crystallographic rotational-translational symmetry operation (-1/2+x, 1/2-y, 1-z). Starred atoms are related to unprimed ones via the crystallographic translational symmetry operation (1+x, y, z). The network propagates as a chain in a direction parallel to the crystal unit cell's a axis.
List of Tables

Table 1. Crystallographic Experimental Details
Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters
Table 3. Selected Interatomic Distances
Table 4. Selected Interatomic Angles
Table 5. Hydrogen-Bonded Interactions
Table 6. Torsional Angles
Table 7. Anisotropic Displacement Parameters
Table 8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms
Table 1. Crystallographic Experimental Details

A. Crystal Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>$C_{12}H_{15}NO_6$</td>
</tr>
<tr>
<td>formula weight</td>
<td>269.25</td>
</tr>
<tr>
<td>crystal dimensions (mm)</td>
<td>$0.67 \times 0.20 \times 0.13$</td>
</tr>
<tr>
<td>crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>$P2_12_12_1$ (No. 19)</td>
</tr>
<tr>
<td>unit cell parameters$^a$</td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.0518 (7)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>10.6100 (12)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>19.603 (2)</td>
</tr>
<tr>
<td>$V$ ($Å^3$)</td>
<td>1258.7 (3)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g cm$^{-3}$)</td>
<td>1.421</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>0.115</td>
</tr>
</tbody>
</table>

B. Data Collection and Refinement Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffractometer</td>
<td>Bruker PLATFORM/SMART 1000 CCD$^b$</td>
</tr>
<tr>
<td>radiation ($\lambda$ [Å])</td>
<td>graphite-monochromated Mo K$\alpha$ (0.71073)</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>–100</td>
</tr>
<tr>
<td>scan type</td>
<td>$\omega$ scans (0.3°) (20 s exposures)</td>
</tr>
<tr>
<td>data collection 2θ limit (deg)</td>
<td>55.02</td>
</tr>
<tr>
<td>total data collected</td>
<td>10987 (-7 ≤ h ≤ 7, -13 ≤ k ≤ 13, -25 ≤ l ≤ 25)</td>
</tr>
<tr>
<td>independent reflections</td>
<td>1686 ($R_{\text{int}} = 0.0284$)</td>
</tr>
<tr>
<td>number of observed reflections (NO)</td>
<td>1494 [$F_o^2 ≥ 2σ(F_o^2)$]</td>
</tr>
<tr>
<td>structure solution method</td>
<td>direct methods ($SHELXD^c$)</td>
</tr>
<tr>
<td>refinement method</td>
<td>full-matrix least-squares on $F^2$ ($SHELXL–97^d$)</td>
</tr>
<tr>
<td>absorption correction method</td>
<td>Gaussian integration (face-indexed)</td>
</tr>
<tr>
<td>range of transmission factors</td>
<td>0.9851–0.9273</td>
</tr>
<tr>
<td>data/restraints/parameters</td>
<td>1686 [$F_o^2 ≥ 3σ(F_o^2)$] / 0 / 175</td>
</tr>
<tr>
<td>Flack absolute structure parameter$^e$</td>
<td>0.3(13)</td>
</tr>
<tr>
<td>goodness-of-fit ($S$)$^f$</td>
<td>1.080 [$F_o^2 ≥ 3σ(F_o^2)$]</td>
</tr>
<tr>
<td>final $R$ indices$^g$</td>
<td></td>
</tr>
<tr>
<td>$R_1$ [$F_o^2 ≥ 2σ(F_o^2)$]</td>
<td>0.0348</td>
</tr>
<tr>
<td>$wR_2$ [$F_o^2 ≥ 3σ(F_o^2)$]</td>
<td>0.0849</td>
</tr>
<tr>
<td>largest difference peak and hole</td>
<td>0.255 and –0.120 e $Å^{-3}$</td>
</tr>
</tbody>
</table>

$^a$Obtained from least-squares refinement of 4995 reflections with $4.36° < 2\theta < 49.78°$.

$^b$Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

(continued)
Table 1. Crystallographic Experimental Details (continued)


\(^e\) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. The low anomalous scattering power of the atoms in this structure (none heavier than oxygen) implies that the data cannot be used for absolute structure assignment, thus the Flack parameter is provided for informational purposes only. The absolute stereochemistry is based on the established stereochemistry of the precursor compounds.

\(^f\) $S = \left[ \sum w(F_o^2 - F_c^2)^2 / (n - p) \right]^{1/2}$ ($n =$ number of data; $p =$ number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0435P)^2 + 0.2454P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

\(^g\) $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|; wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$. 
<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.1510(2)</td>
<td>0.14703(14)</td>
<td>0.31987(6)</td>
<td>0.0318(3)*</td>
</tr>
<tr>
<td>O2</td>
<td>-0.3947(2)</td>
<td>0.20477(18)</td>
<td>0.27583(7)</td>
<td>0.0433(4)*</td>
</tr>
<tr>
<td>O3</td>
<td>-0.3494(2)</td>
<td>0.22004(14)</td>
<td>0.41716(7)</td>
<td>0.0334(3)*</td>
</tr>
<tr>
<td>O4</td>
<td>0.2251(2)</td>
<td>0.16874(14)</td>
<td>0.46048(6)</td>
<td>0.0335(3)*</td>
</tr>
<tr>
<td>O5</td>
<td>0.6059(3)</td>
<td>-0.43315(17)</td>
<td>0.38537(11)</td>
<td>0.0596(5)*</td>
</tr>
<tr>
<td>O6</td>
<td>0.2775(4)</td>
<td>-0.50817(18)</td>
<td>0.39355(14)</td>
<td>0.0812(7)*</td>
</tr>
<tr>
<td>N</td>
<td>0.4066(4)</td>
<td>-0.42043(19)</td>
<td>0.39267(11)</td>
<td>0.0460(5)*</td>
</tr>
<tr>
<td>C1</td>
<td>0.0732(3)</td>
<td>0.1836(2)</td>
<td>0.25299(9)</td>
<td>0.0328(4)*</td>
</tr>
<tr>
<td>C2</td>
<td>-0.0511(4)</td>
<td>0.3063(2)</td>
<td>0.25741(10)</td>
<td>0.0368(5)*</td>
</tr>
<tr>
<td>C3</td>
<td>-0.2463(4)</td>
<td>0.2939(2)</td>
<td>0.30542(10)</td>
<td>0.0354(4)*</td>
</tr>
<tr>
<td>C4</td>
<td>-0.1641(3)</td>
<td>0.24768(18)</td>
<td>0.37450(10)</td>
<td>0.0284(4)*</td>
</tr>
<tr>
<td>C5</td>
<td>-0.0277(3)</td>
<td>0.12737(18)</td>
<td>0.36592(9)</td>
<td>0.0255(4)*</td>
</tr>
<tr>
<td>C6</td>
<td>0.0723(3)</td>
<td>0.08072(19)</td>
<td>0.43339(9)</td>
<td>0.0282(4)*</td>
</tr>
<tr>
<td>C7</td>
<td>0.1671(3)</td>
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<td>0.42476(9)</td>
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</tr>
<tr>
<td>C8</td>
<td>0.3819(3)</td>
<td>-0.0702(2)</td>
<td>0.40142(10)</td>
<td>0.0321(4)*</td>
</tr>
<tr>
<td>C9</td>
<td>0.4589(4)</td>
<td>-0.1911(2)</td>
<td>0.39002(10)</td>
<td>0.0349(5)*</td>
</tr>
<tr>
<td>C10</td>
<td>0.3214(4)</td>
<td>-0.2918(2)</td>
<td>0.40256(10)</td>
<td>0.0342(4)*</td>
</tr>
<tr>
<td>C11</td>
<td>0.1076(4)</td>
<td>-0.2761(2)</td>
<td>0.42607(10)</td>
<td>0.0367(5)*</td>
</tr>
<tr>
<td>C12</td>
<td>0.0340(3)</td>
<td>-0.1537(2)</td>
<td>0.43720(9)</td>
<td>0.0342(5)*</td>
</tr>
</tbody>
</table>

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^*a^2U_{11} + k^2b^*b^2U_{22} + l^2c^*c^2U_{33} + 2hkc^*c^*b^*U_{23} + 2hlac^*c^*b^*U_{13} + 2hka^*b^*a^*U_{12})]$. 
Table 3. Selected Interatomic Distances (Å)

<table>
<thead>
<tr>
<th>Atom1</th>
<th>Atom2</th>
<th>Distance</th>
<th>Atom1</th>
<th>Atom2</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
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Table 6. Torsional Angles (deg)

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The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hkl^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$
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<th>( z )</th>
<th>( U_{eq} ) Å²</th>
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Table 8. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms